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REPORTS

OF THE

PROGRESS OF APPLIED CHEMISTRY.

PLANT AND MACHINERY

By J. W. Hinchley, A.R.S.M., Wh. Sc., F.I.C.,
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Perhaps in no department of activity has so much progress been made through the war as in chemical engineering. It is difficult and in many cases undesirable to give a complete account of the new developments that have taken place in the industry through the necessity of success in the war and freed from the factor of uncertain competition.

Continuous processes and plant have supplanted familiar discontinuous methods, new materials have come into general use, and improvements of local materials of all kinds have been made to meet the needs of the chemical engineer.

The best chemical stoneware was formerly obtained from Germany by chemical manufacturers all over the world. Several manufacturers in this country and in America now claim, with substantial reason, that their products have never been surpassed. Other makers are turning out chemical stoneware of satisfactory quality for the uses to which it may be put, but frankly admit that they are still on the road of improvement.

Perhaps it is more to be remarked that the designs of our manufacturers of pipes, condensers, injectors, cocks, etc., show a considerable advance on pre-war practice. The use of the diamond tool in producing true working faces in stoneware has made cocks and similar fittings of some makers more reliable than was formerly thought possible.

Silica ware, which had definitely established its position seven years ago, has continued to be of the greatest possible service in the production of pure acids. Closed cascade basins of this material are now used for the denitration of mixed acids. Pot coolers for concentrated sulphuric acid are nearly universally made of this material. Retorts up to 75 litres capacity have made possible larger scale operations on certain pure materials, than formerly. Owing to the small coefficient of expansion and somewhat brittle character of silica, worms and cooling pipes are usually exposed to the air and cooled by water trickling over them; fractures and leaks are thereby readily detected.

Ceratherm is a new material which is similar to silica ware in having a low coefficient of expansion, but is capable of standing greater stresses and replacing stoneware in difficult situations. It is useful for first condensing vessels and pipes in positions where the temperature and other conditions are severe, and where its first cost is justified. Centrifugal pumps of this material (armoured) are said to be very successful.

The use of brickwork in chemical plant construction has increased enormously, and the reliability of certain new cements has enabled manufacturers to do without any sheet lead covering which was formerly necessary. The well known brands of blue brick, metalline, obsidianite, iron, &c., have retained their high character, and several new brands have also appeared. The great success which has attended the construction of scrubbers, concentrators, and other plant working under comparatively high temperature conditions in the concentration of sulphuric acid and similar processes, of cemented brickwork with little or no metal protection or support, has been due to the scientific use of certain cements which have been known for some time, but which were not understood. One of the most successful of these cements[1] consists of acid-resisting siliceous material mixed with a very small proportion of calcium sulphate, and made into a thin paste with sodium silicate solution. After the brickwork is completed the structure is exposed for a few days to a temperature of about 100° C. or more. With good foundations, solid design, and well made plant of this nature, no failure through cracks or other defects takes place, and the size of units may be enormously increased with a consequent lowering of the cost of production.

Chemical cast iron has become better known during the last few years, although the importance of using a special material for chemical purposes, even now, is not properly appreciated. In spite of the development of acid resisting irons, chemical cast iron is likely to remain the best material for nitric acid stills and similar purposes, while for general construction it must continue to be the most important material of the chemical engineer.

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[1] Chance and Hunt, Holley and Webb, Eng. Pat. 110258, 1917; J., 1917, 1237.

Evaporators with tubular heaters for corrosive and other solutions, such as ammonium nitrate, caustic soda, &c., which necessitate the use of chemical cast iron, have been improved greatly. A very efficient type,[2] using very long tubes, has been made more efficient and given a longer life by the invention of a method of casting very long, small-bore cast iron tubes. Formerly such tubes were made of suitable length by means of wrought iron sockets, so that the life of the tube was determined by the life of the sockets, while the number of tubes which could be used in a given space was reduced. Homogeneous cast iron pipes of 2 inches bore and about 15 feet long are now made by well-known cast iron founders by means of an ingenious method of supporting the cores. It is, of course, well understood that the use of metal chaplets to support the core or of any material which remains in the metal is out of the question on account of the rapid corrosion which would occur.

The highest qualities of cast iron ("shell container" or "semi-steel" quality) have been found of great value in substitution for steel where the conditions have not been too severe. High pressure apparatus of steel can now be made without the trouble formerly experienced. Electric steel castings are also available and autoclaves of forged or cast metal are readily made. Anti-corrosive steels and self-hardening steels, in which great advances have been made, are often of value to the chemical engineer for stirrers, rabbles, and rakes in furnace operations.

The most important recent alloy is iron silicon, which is sold under the trade names Tantiron, Duriron, Ironac, Narki, &c. The best brands of this alloy contain about 15 % of silicon with minimum quantities of other substances, especially graphite and phosphorus. The tensile strength of simple cast rods is about three quarters of that of cast iron, but owing to its high shrinkage its strength in use cannot be relied upon except for the smaller and simplest castings. Unfortunately most castings are porous just below the skin, and this porosity is often the cause of failure in use. Its resistance to corrosion by nitric and sulphuric acids is so remarkable that it has rapidly established itself as a standard material for these substances. Pipes, cocks, coolers, nitric acid condensers, &c., which were formerly made in stoneware, are now commonly made in iron silicon and on account of their higher heat conductivity and greater strength, show important economic advantages.

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[2] Kestner "climbing-film" evaporator.

Unfortunately the metal cannot be machined except with great difficulty, but mercury hardened drills are often capable of producing a satisfactory hole. The working faces of cocks and valves and similar true surfaces are produced by grinding with emery wheels. Basins for use in the cascade system of sulphuric acid concentration have been made for some time in this material but recently plants with basins 3 feet in diameter have displaced those taking the ordinary 12-inch size. Plunger pumps and fans are also made in iron-silicon alloy, and in some cases have been successful, while in others fracture of the castings has been a continuous source of trouble. With careful design to avoid shock and vibration, a flexible drive good workmanship and material, there is no reason why these machines should not be always successful. The alloy does not resist hydrochloric acid or chlorides well.

Many other acid-resisting alloys have been proposed and a few very expensive ones have come into successful use. Nickel containing from 15 to 50 of chromium resists nitric acid perfectly, is very ductile, can be forged, and has a high tensile strength (50 tons per square inch or more). It does not form a scale when heated to redness, and has the highest ' red-hardness ' of all alloys. It is an excellent substitute for platinum in many plants, especially catalytic chemical plants. The success in recent years of the electric stove, electric laboratory furnaces, hot plates, etc., is due to the excellent properties of this material. Unfortunately, it is slowly attacked by hydrochloric, sulphuric, and hydrofluoric acids.

Acid-resisting aluminium alloys generally owe any good qualities they possess to the presence of a small percentage of chromium (less than 1).

Platinum substitutes have also appeared which are alloys containing gold and palladium.

Although the improvements made in plant during the last few years have been very great indeed, at the same time on account of the market conditions, there has come into use in non-munition industry a very large amount of plant of the crudest and most unsatisfactory kind, which will be scrapped as soon as the war is over. Most of the improvements have been made by the application of well-known scientific principles, and as a result of the industry being dependent upon itself for its equipment. Plant, which was formerly of foreign origin, has been made on the spot, and in many cases of enormously increased efficiency.

The ' Kek ' disintegrator has become very popular on account of its simple design, convenience in use, and high efficiency. It is a horizontal disc disintegrator with an enclosed spiral gear drive.

Excellent discontinuous and continuous ball mills are now made wholly in Britain. Formerly even the American makers imported German porcelain bodies. An ingenious modification of the ball mill has come into considerable use. The trunnions are made hollow so that treatment with gases or vacuum drying may be carried out during the grinding operation.

Several new roasting furnaces have recently been put to work. A mechanical salt-cake furnace,[3] specially adapted for the treatment of common salt with nitre cake for the production of hydrochloric acid, should be mentioned. A series of rabbles of high-speed steel, fixed to a frame, are reciprocated by means of an electro motor, stirring up the material during the reaction and gradually pushing the exhausted mass to the exit of the furnace, where a screw conveyor removes it; the rabbles are bent towards the exit to secure this result. On account of the increasing reliability of the rotary mechanical pyrites burner large numbers have been installed both with air- and with water-cooled arms. By arranging the lower hearth as a muffle heated by producer gas, coal or oil fuel, such burners have been perfectly adapted for roasting blende. The popularity of these furnaces may be readily understood from the fact that the power required is less than ½ h.p. per ton-day output, one man can attend to six or more furnaces, repairs cost about 2*d*. per ton, and rich gases are readily produced. A simple mechanical muffle furnace with one hearth of similar design for special roasting operations has also been introduced.

In evaporating and distilling plant great strides have been made by the application of scientific principles. It is now well understood that liquids and gases are very bad conductors of heat, and that the most efficient heating methods involve either radiation or mechanical transmission. The Bonecourt system of surface combustion is an example of the former method, and film, spray, and similar evaporators are examples of the latter. The more violent the agitation of the heated and heating fluids, the more efficient will be the heat conduction. By lowering the static level of the liquid in ordinary evaporators the evaporation may often be increased as much as 50%, and in the climbing film evaporator, in which velocities of over 200 feet per second are obtained, the effect of high velocity of the heated fluid on the heat transmission is very pronounced.

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[3] Six and Guttmann, Eng. Pat. 4226, 1915; *J.*, 1916, 821.

In multiple effect evaporation an average temperature difference of about 30° C. has been usually considered the most efficient practice in that the plant charges, first cost, repairs, and depreciation are not immoderate. In recent years ten effect plants, with average temperature differences of about 15° C., have come into use in operations not involving serious corrosion. A new departure has now been taken on the lines suggested by Siemens in 1868, and has been carried to practical results.

Working with very small temperature differences (2° to 5° C.), with film, spray, or similar method of supplying the liquid to the heating surface, it is possible to compress efficiently the vapour given off so as to raise its temperature to that of the heating steam. Two systems of doing this have been devised. In one the increased pressure is obtained by means of a turbine fan,[4] and in the other by means of a steam jet,[5] the steam supplied being the heating steam from the boiler. It is obvious that the entering liquor can be heated to near the evaporation temperature by a heat exchanger receiving the condensed water. The turbine fan method presents the least mechanical difficulty and the highest efficiency, but the steam jet method may be more suitable for chemical purposes.

The efficiency of such evaporators is remarkable, single-effect evaporators giving results superior to those of ten-effect evaporators of normal type. Used in conjunction with a "finisher," they may displace multiple plants for many purposes.

A very efficient form of heating surface for stills for chemical work is formed by a bank of horizontal field tubes.[6] The tubes are fixed at one end and closed at the other, steam being supplied through an inner tube, so that they are easy to replace and give a high coefficient of heat transmission.

A simple crystalliser to handle the concentrate from the "finisher" consists of an inclined cooled rotating cylinder provided internally with a fixed scraper to detach the crystals as they form.

A number of attempts to avoid back pressure in the rectifying columns of stills have been made without efficient result. The provision of spirals of increasing twist[7] in the heating tubes of stills and condensers is found to give increased heat transmission by increasing the agitation of the fluids. Such spirals used in nitric acid condensers have been of value.

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[4] Soderlund and Boberg evaporator.

[5] Prache and Bouillon evaporator.

[6] British Dyes Ltd., Metcalf, and Welch, Eng. Pat. 10,909, 1916; *J.*, 1917, 537.

[7] Goodwin and Guttmann, Eng. Pat. 14,165, 1915; *J.*, 1916, 1145.

Scrubbers and washers are of great interest to the chemical engineer. Filling materials are constantly being devised to meet his demands and ideas. The well-known good properties of coke as a filling material have been imitated by an artificial pumice stone produced by melting glass with a small percentage of carbon. Of filling materials made of stoneware, blue-brick, and similar materials, "propeller," "E B R," "diabolo," and many other cell forms have become popular. Tubular scrubbers have also been introduced with success.

Several developments in gas washers and scrubbers have been made. In mechanical washers, the use of a stuffing box for the rotating shaft may be avoided by providing a deep collar on the shaft working in a deep groove next the bearing inside the casing. The washing liquid being continually thrown from the edge of the collar into the recess, forms an excellent seal to the washer,[8] which is free from the friction and wear and tear of a stuffing box.

The space-surface advantages of an annulus have been made use of in a gas washer and cooler[9] in which the gas is subjected to sprays of water while in the annular spaces of a tubular apparatus. A single form of atomiser has been introduced which is especially useful for thick liquids, and is provided with lateral jets to break up the annular stream before it reaches the main atomising jet.

The Cottrell or similar apparatus for the electrical deposition of fume and dust has been adopted in several chemical plants. For the deposition of fume from Gaillard and other concentrators, phosphoric acid and similar plants, the apparatus has been very successful. Where, however, solid as well as liquid particles are present, the plant is not so well thought of. At one concentrating plant about 25 tons of 40 % to 50 % sulphuric acid is recovered daily from the fume. With dry dust such electrostatic plants give very good results, especially in cement and similar industries.

The Gaillard concentrator for sulphuric acid has become a standard plant for large outputs, as the Kessler plant is for moderate outputs, the cascade plant being only useful for small outputs. The Harris-Thomas plant, in which the concentration is carried out in silica ware tubes, appears likely to become a serious competitor to the latter. The Gilchrist concentrator, consisting of an overheat concentrating pan with a simple scrubbing tower for the effluent, is also a simple plant suitable for medium outputs. For phosphoric acid concentration it would appear to be very well adapted.

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[8] Davis, Eng. Pat. 104465, 1916; *J.*, 1917, 447.

[9] Christopher, Eng. Pats. 10040, 1915, and 103561, 1916; *J.*, 1916, 914; 1917, 332.

In filtration plant some advances have been made but the most noticeable feature of recent times is the enormous home manufacture of the ordinary filter press. The mechanical accuracy of the plates and frames of such presses often determines their efficiency in use. With truly parallel plates and frames the pressure is evenly distributed over the jointing faces, and the life of the filter cloth is a maximum from that point of view. Truly parallel plates and frames can only be made on commercial lines by machining both sides of the plate or frame at one operation, preferably in a double-headed facing lathe holding the plate stationary between the cutting heads.

The use of fired porous clay for filtration has increased greatly and filters specially adapted for its use have become standard plant. For very fine precipitates in acid solutions such filters are most satisfactory. The filtering surface is practically permanent and does not clog, so that the same filtering efficiency is always obtained. This filter usually consists of a lead-lined steel cylinder carrying a number of filtering trays which can be moved on rails into and out of the cylinder. Outlet pipes from the trays, with temporary joints in the cylindrical shell, provide for the outlet of filtrate. The trays are filled with the sludge to be filtered, and compressed air is admitted to the cylinder after making the joints; on admitting water to the trays the cakes can be washed before opening the cylinder for their removal.

In presses having cages for the removal of liquid from plastic or other materials some important development has taken place. Delicate filtering surfaces can be protected by coarsely-perforated plates to support the pressure, the material "arching" over the holes and effectively relieving the filtering surface. The filtering is thus carried out at low pressure while the mass is being submitted to a much higher one. Porous filtering tiles have been used in such presses with pressures up to half a ton per square inch.

Among subsidiary steam plant an interesting steam trap must be mentioned called the "dynamic impulse steam trap." In other steam traps the water discharge is determined either by the contraction of parts through the cooling effect of the condensed water, or by the accumulation of condensed water actuating a float. In this trap a water-hammer action opens the discharge valve in a series of pulsations.

Adequate regulation of steam boilers to give the highest duty has received a great deal of attention. Simple automatic proportional regulation of the feed-water to meet sudden demands for steam is obviously unsatisfactory. Fluctuations in the level of the water in the boilers should occur in some relation to the maximum and minimum demand for steam, so that an increase in load should be accompanied by a relative decrease in feed and a decrease in load by a relative increase in feed, the water level rising or falling with a decrease or increase in load respectively. Regulators for this purpose are being installed in works where fuel control was formerly unheard of.

A simple form of regulator (Copes) consists of an inclined tube placed at the water level and connected to the steam and water space of the boiler. Expansion or contraction of this tube through the presence of steam or water actuates a lever controlling the feed. The upper and lower ends of the expansion tube correspond to the maximum and minimum water-levels, and the time lag which occurs in its action becomes a valuable source of thermal storage to meet sudden loads.

FUEL

By J. S. S. Brame

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Coal

Constitution

There is little to record in connection with the extension of the knowledge of the composition of coal. R. V. Wheeler summarised recent work on the subject before the London Section of the Society, and Marie Stopes gave an interesting account of the palæbotany of coal.[1] These papers were discussed by the Newcastle Section,[2] when J. T. Dunn summarised the present state of our knowledge of the constituents of coal as practically negligible and no greater than it was in 1908, after Bedson published his results on pyridine treatment. The only new step seemed to be Wheeler's extraction of the pyridine extract with chloroform, by which the separation of this extract into two characteristically different bodies was accomplished. One of these appears to be of resinic origin, the other a degradation product of cellulose previously regarded as not soluble in pyridine.[3]

A. Wahl[4] has further examined the action of pyridine and quinoline as solvents, with results generally in agreement with other work; the pyridine extract had practically the same ultimate composition as the original coal. Wahl also examined the coals on the lines of metallographic analysis, a method suggested by the writer in 1916 as likely to afford valuable information. A polished surface was etched with pyridine. F. Fischer and W. Gluud[5] extracted lignites with liquid sulphur dioxide and obtained typical resinous substances.

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[1] See Supp. to *J.*, p. 5, Jan. 31st, 1917.

[2] *J.*, 1917, 176.

[3] Wheeler and Clark, *Chem. Soc. Trans.*, 1913, **103**, 1704; *J.*, 1913, 969.

[4] *Bull. Soc. Chim.*, 1917, **21**, 76; *J.*, 1917, 634.

[5] *Ber.*, 1916, **49**, 1469; *J.*, 1916, 1001.

Terres[6] has investigated the condition in which nitrogen probably exists in coal. By distillation of a number of nitrogen compounds of different character he found that amines or substituted amino-compounds were the only ones yielding ammonia, and concluded that the nitrogenous ammonia-yielding constituents of coal were protein in character. When coal is coked from 10–40% of the nitrogen remains in the coke; this is concluded to be in the form of nitride, and 90% is recoverable as ammonia on gasification.

The condition in which water exists in coal was the subject of an important paper by E. Mack and G. A. Hulett.[7]

Deterioration and Spontaneous Ignition of Coal

The effect of storage upon the properties of coal has been further studied by S. W. Parr.[8]

The work has been a continuation of experiments on "The Weathering of Coal,"[9] "The Occluded Gases in Coal,"[10] and "The Spontaneous Combustion of Coal."[11] For the work on "The Weathering of Coal," car-lot samples were stored for one year. The investigation was continued for five years longer, when the coal was used in boiler tests to establish the character of the various samples. The most serious part of the problem of coal storage relates to the matter of spontaneous heating, and probably the least serious part to deterioration and actual loss of heat value. The general conclusions as to oxygen absorption are confirmatory of other recent work, including that of the author and his colleagues, but particular interest attaches to the further information available on the part played by pyrites, a subject investigated by Winmill and dealt with in last year's Report. Parr estimated the sulphur in the sulphuric anhydride form in samples at the time of grinding and some six months later, at the same time tracing the effect of fineness of division on the rate of change. The growth of sulphate is shown in the table on p. 18.

With one exception the coarse, or 10-mesh, material showed little or no indication of sulphur oxidation, whilst with fine division five out of seven samples show that oxidation occurs at room temperatures. Further tests emphasised the fact that oxidation of sulphur increased in activity as the size of the particles decreased and the superficial area in any given mass correspondingly increased; also that free moisture was an important factor. Samples in which both the water and the sulphur contents were high, showed an increase in the sulphur oxidation over those samples low in water and sulphur.

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[6] *J. Gasbeleucht.*, 1916, **59**, 519; *J.*, 1917, 559.

[7] *Amer. J. Sci.*, 1917, **43**, 89; *J.*, 1917, 378.

[8] *Bull. No.* **97**, *Eng. Experimental Station, Univ. of Ill.*

[9] *Bull.* **38**, 1909.

[10] *Bull.* **32**, 1909.

[11] *Bull.* **46**, 1910.

Moisture. Per cent	Total sulphur. Per cent.	SO_3 60-mesh, August, 1912. Per cent	SO_3 60-mesh, April, 1913 Per cent	SO_3 10-mesh, April, 1913. Per cent
6·33	5·29	0·95	1·16	0·86
8·94	2·27	0·39	0·38	0·18
4·49	4·92	0·47	0·49	0·25
4·86	5·16	0·63	1·25	1·12
7·66	8·73	0·61	1·12	0·86
7·93	5·20	1·42	1·79	0·82
8·05	4·83	0·62	1·20	0·81

In summarising his conclusions regarding spontaneous heating, Parr concludes that the oxidation of organic material in freshly mined bituminous coal is active, the action increasing with fineness of division and increased temperature; he gives first place in time and effect to this action. Oxidation of sulphur in the form of pyrites is active in presence of moisture and when there is fineness of division, but this latter action waits somewhat upon the rise of temperature due to organic oxidation before the action with sulphur reaches a serious phase. It is true also that a coal may heat seriously even though pyritic sulphur is absent.

The loss of heating value is most rapid during the first week, when the average loss is about 1%; additional loss of from 2 to 3% may occur by the end of the first year. At the end of six years the indicated losses in some cases equalled nearly 11%. A study of the relative ash values corresponding to the various stages of indicated heat losses reveals a constant lowering of the percentage of ash, this being due to increase of weight of the mass with apparent decrease of ash.

These facts seem to afford basis for the statement that the actual heat losses in stored coal are apparent rather than real; the true heat losses are those due to escaping gases and the heat generated by direct combination with oxygen. Both of these are held to be practically negligible.

The increase of weight on storage was found to be greater in covered bins than in the open, so that coal stored in the open showed a lower loss of heating value than when stored under cover. The leaching out of soluble matter in the open accounts for this.

The breaking down of coal on storage is a recognised action, leading to considerable increase in small coal. After one and a half years the amount of coal passing a ¼-in screen increased 11% - 17%, after six years, 12·6% to 31%. The process of oxidation of organic matter may be as responsible for this breaking down as the oxidation of finely divided pyritic sulphur.

Boiler tests on the weathered coal showed that a stronger draught was required, not necessarily due to a high dust factor. It would appear that oxygen absorption leads to a slower rate of combustion. Burning weathered coal is largely a question of correct handling and ignition. Fires should be thinner, the draught should be greater, and it was found that the fuel bed should not approach nearer to the water-back than from 4 to 6 in., otherwise trouble is experienced with clinkering. Under suitable conditions practically as high capacity and over-all efficiencies could be obtained with weathered coal as with fresh screenings.

The influence of pyrites on the oxidation of coal was also investigated by T. J. Drakeley,[12] who showed that pyrites has a minor effect on the oxidation of coal; it is a subsidiary factor, but cannot be ignored.

A further paper by Drakeley[13] deals with the liberation of hydrogen sulphide from gob fires in coal mines. The author says that the evolution of this gas from such fires is undoubted, and concludes that it might be formed by reduction of sulphur dioxide by the hot coal. To test the point sulphur dioxide was passed in a stream of moist carbon dioxide over coal heated to 500° C., the tar removed and the gases passed through concentrated sulphuric acid, the hydrogen sulphide being quantitatively estimated by absorption in acid copper sulphate. The quantitative results are open to question, for it is well known that the gas is decomposed by sulphuric acid with the liberation of sulphur; indeed in experiments with coal and sulphur the author mentions accumulations of sulphur in the sulphuric acid wash bottle.

Drakeley has, however, shown that hydrogen sulphide is evolved by simply heating coal; by passing sulphur dioxide over heated coal; by heating coal with sulphur or pyrites; by passing water vapour or hydrogen over heated pyrites. Moisture is found to play an important part in all these reactions.

The experiments are held more particularly to refute a conclusion arrived at by V. B. Lewes, that iron pyrites had no connection with the spontaneous heating of coal because in one case of spontaneous combustion sulphur was evolved as hydrogen sulphide and not as sulphur dioxide, "as would be expected if sulphur had anything to do with the fire." Drakeley's results certainly contradict such an assumption, but this was only one link in a chain of evidence against any important action of iron pyrites. Lewes recognised the possible action of pyrites, which, he pointed out, might, under suitable conditions, give rise to ferrous sulphate and sulphur dioxide, with liberation of free sulphur, which element would play an important part in lowering the ignition point. Lewes called attention to the fact, often overlooked, that oxidation of sulphur took place at as low a temperature as 60° C., and concludes "the only way in which pyrites can assist the spontaneous ignition of coal is that when it oxidizes it helps the general rise of temperature, and by swelling splits up the coal, thus exposing fresh surfaces to the action of atmospheric oxygen." The large amount of research work on the subject in recent years has not in any way contradicted this statement.

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[12] *Chem. Soc. Trans.*, 1916, **109**, 723; *J.*, 1916, 1001.

[13] *Chem. Soc. Trans.*, 1917, **111**, 853; *J.*, 1917, 1089.

COMBUSTION OF COAL

An elaborate research on the combustion in the fuel bed of hand-fired furnaces was carried out by H. Kreisinger, F. K. Ovitz, and C. E. Augustine.[14] Two thicknesses of fuel bed were employed, 6 in. and 12 in., and three fuels, bituminous coal, coke and anthracite. The rate of combustion was varied from 20 lb. to 185 lb. of fuel per sq. ft. of grate per hour. Three zones were distinguished in the fuel bed, though these were not well defined, as there was naturally overlapping. The zone nearest the grate comprised that in which oxidation of carbon to carbon dioxide took place, the maximum percentage of this gas being 12% to 18% at a height of 2 in. to 3 in. above the grate. With a 6-in. fuel thickness, and using bituminous coal or anthracite, all free oxygen was used up at 3 in. to 4½ in. above the grate. With coke of the same thickness the oxygen had not all disappeared until a height of 4½ in. to 6 in. was reached. With 12 in. beds of coal and anthracite the results were similar. The maximum temperatures attained ranged from 1120° C. to 1500° C., and were reached at about the same height as maximum carbon dioxide.

The middle zone is one where reducing actions predominate, the carbon dioxide being reduced to monoxide. The rate of reduction is dependent on temperature and time of contact (as is well known in the case of gas-producer practice) equilibrium being rapidly established for the components carbon dioxide and monoxide and carbon at the high temperature of the fuel bed At about 1350° (the mean temperature of the hot zone) contact for 4 seconds would ensure conversion of 98 % to carbon monoxide This reducing zone extends almost to the surface of the fuel bed.

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[14] U.S. Bureau of Mines, Tech. Paper 137; J., 1917, 949.

An important observation was that the fusion of ash to clinker took place in this reducing zone, the half-molten, sticky mass sinking towards the grate then solidified although actually passing into a region where the temperature was at the highest Fieldner and Hall[15] and Fieldner and Feild[16] found that the fusion of coal ash took place at lower temperatures in a partly reducing atmosphere than in either a strongly reducing or oxidizing one

The upper zone was a distillation one, the volatile products from the fuel being driven off This extended for about 2 in from the surface, and was considerably overlapped by the reducing zone.

At the surface of the bed there was always from 20% to 32% of combustible gas present The tar and soot drawn off with the gas were separated, and their weight compared with that of the combustible gases. Approximately the tar and soot comprised about 25% of the total combustible rising from the bed, and in a form difficult to burn in the combustion space If proper provision is not made for its combustion this may go off to the chimney as dense smoke. In some cases the tar amounted to over 60% of the total tar and soot, whilst in the case of smoke collected from the chimney of a hand-fired tubular boiler there was only 3% to 6% tar This is said to indicate the decomposition of the tar into gases and soot as it passes through the furnace, but probably there is a good deal of incomplete combustion of the tar with liberation of free carbon

Most interesting results were found with variation of the air supplied through the grate. Within wide limits this had no effect on the composition of the gases in the fuel bed, which remained practically constant in composition no matter how much air was forced through The rate of air supply through the grate affected the rate of combustion in direct proportion, the weight of air used per lb of combustible being constant for all rates. Under no conditions of forced air supply was there any free oxygen for the combustion of the gases escaping from the top, so that all air for this purpose must be supplied above the grate, and the regulation of this air can alone determine the percentage of carbon dioxide in the flue gases. With bad firing, leading to holes in the bed, badly fitting doors, or leaky brickwork, so much air may get into the combustion space as to lead to the erroneous idea that air supply over the grate is sometimes unnecessary.

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[15] *J. Ind. and Eng. Chem.*, 1915, 7, 399; *J.*, 1915, 704.

[16] *Loc. cit.*, 1915, 7, 742; *J.*, 1915, 1001.

The ideal way to supply additional air over the fuel bed is to introduce it as close to the fuel bed as possible, thus more combustion space is utilised for mixing and burning the mixture. Mixing will of course be best secured by dividing the air into as large a number of small streams as possible.

Interesting results were obtained for the pressure drop through the different fuel beds. The three fuels—bituminous coal, anthracite, and coke—were all sized to pass through a $1\frac{1}{2}$-in. screen and over a 1-in. screen. The pressure drop with the coal and coke showed no appreciable difference, but the drop was much higher with anthracite. The increased resistance thus indicated was ascribed to the breaking up of the anthracite into small pieces under the action of heat, and the important conclusion is reached that the resistance of the fuel bed to the flow of air depends not only on the size of the fuel but to an even larger extent on its nature, an important fact to be taken into consideration in estimating the rate of combustion for different coals for a given available draught.

A paper on "Coal efficiency in the boiler house," by T. G. Otley and V. Pickles,[17] is noteworthy for describing the conditions for the satisfactory use of very high ash coals containing a large amount of duff. Such poor fuel is not important in this country at present, but may become so at a future date, as our better-class coals are reduced and prices become higher. Screening tests showed that from 50% to over 60% of the duff passed a $\frac{1}{8}$-in. mesh sieve, and 32–44% over $\frac{1}{8}$-in. and through a $\frac{1}{4}$-in. mesh sieve. At one time attempts to burn such duff on a chain-grate stoker alone and dry resulted in 70% riddling through the grate. To burn duff satisfactorily it should be evenly mixed with other coal, but bunker arrangements often preclude this. It is generally recognised that duffs burn better wet; unless wet it goes over the grate like a blanket, giving a low furnace temperature, and if the draught is increased unduly, the fuel bed is broken up into ridges through which large volumes of excess cold air enter the furnace, lowering the efficiency. The writers suggest that "there may be some chemical explanation of the advantage of wetting, but no doubt some portion of the improvement is due to the moisture expanding and moving the particles of coal apart, thus allowing more even access of air through the fuel bed." Dry duff may give only 6 % of carbon dioxide in the flue gases, but by wetting the carbon dioxide may be raised to 10·5 %–12 %. One coal in constant use contained 32·5 % of ash, and this is considered the practical limit for burning commercially on chain-grate stokers. This coal often had the low calorific value of 7500–7700 B.Th.U. per lb. The conditions necessary for burning this type of coal are (1) proper arch design, (2) suitable grading, (3) proper draught, (4) thorough saturation with water. With the standard arches the coal could not be got to ignite regularly, and grates had to be run so slowly that normal evaporation could not be obtained, and the thickness of the fires had to be increased considerably. The arches were increased in length, raised several inches, and made higher at the back than at the front.

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[17] *J. S. African Inst. Eng.*, Jan., 1917; see *Engineer*, 1917, **123**, 116, 137.

The authors lay great stress on external cleanliness of the tubes, &c.; they consider this of more importance than a layer of scale of any reasonable thickness on the inside of the tubes, and as the dominant factor affecting evaporation output. With duff it is an absolute necessity to soot the boilers and economisers thoroughly with every five hundred hours' running.

As showing the advantage of this cleansing the following results, each on a 12 hours' test, may be cited:

	Before cleaning lb.	After cleaning lb.
Coal burnt per sq. ft. grate	68,400	72,000
Coal per sq. ft. per hour	22·6	23·8
Lb. water evaporated per lb. coal (actual)	6·86	7·09
Boiler efficiency	75·1	78·7

Pulverised Fuel for Heating and Steam Raising

The use of powdered coal has attracted very considerable attention in the United States. The possibilities of dust firing are well recognised, for it is probably the most scientific method of burning raw coal, and the utilisation of fine coal (which can with fair ease be further reduced to the necessary degree of fineness; this is often dangerous by reason of its liability to spontaneous ignition and is of little value because of the difficulty of burning on a grate or gasifying in a producer) is a matter of considerable economic importance. Such fine coal is, however, usually high in ash, and this constitutes one difficulty from slag and dust deposits in flues, &c.

Very satisfactory results have been obtained on railways in the United States with powdered coal. In an article on its use for locomotive firing, J. E. Muhlfeld[18] regards it as a competitor with electric traction, indeed as superior for long distance traffic, for here the use of electricity is precluded by reason of high first cost, fixed charges, maintenance, &c. Besides eliminating smoke, dust firing was found to give increased thermal efficiency, and excellent results are claimed to have been obtained as regards tonnage, speed, combustion, and steam pressure. Satisfactory results were also obtained with powdered lignite.

Muhlfield says that the fuel should not contain more than 1% moisture, and after grinding 9[illegible]% should pass a 100-mesh sieve and 85% a 200-mesh sieve. With suitable arrangements for storage 15 tons of the powdered fuel can be delivered from overhead bins into the tender in from three to four minutes.

In this connection mention may be made of the use of powdered peat as locomotive fuel on the Swedish State Railways.[19] In comparison with coal, peat gave very satisfactory results. With respective calorific values of 7740 B.Th.U. for peat and 12,600 B.Th.U. per lb. for coal, the average kilos. of steam per kilo of coal were peat, 4·71; coal, 6·81. The boiler efficiencies worked out at 73% for peat firing and 65% for coal. The equivalent of peat to coal as unity came to 1·45 lb. Considerably higher fire-box temperatures were obtained for peat (1670° C. peat, 1510° C. coal). The peat powder was carried in a hopper with conical bottom and blown into the furnace over a small coal fire placed beneath the delivery nozzle. The coal consumption amounted to 3%–4% by weight of peat.

In America also the possibilities of powdered coal for furnace work have received attention. In connection with open-hearth steel furnaces, J. W. Fuller[20] claims that it gives a more regular supply of heat than producer gas, that it is much easier to powder and burn coal than to gasify it, and that the first cost of producer plant is eliminated. Fuel consumptions compare very favourably with the best producer practice, it being claimed that from 100 lb.–150 lb. less coal per ton of ingots cast is required. The steel output is increased from 10%–40%, and there is 1%–2% less loss by oxidation of pig iron and scrap in melting down.

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[18] *Amer. Soc. Mech. Eng.*, see *J.*, 1917, 75.

[19] *Engineering*, 1916, **102**, 387; *J.*, 1916, 1097.

[20] *Amer. Iron and Steel Inst.*

Slag is the greatest difficulty and necessitates specially designed checkers and provision of slag pockets The ash of the coal must be low and high bituminous matter is necessary.

A paper by C A King[21] records results of dust firing with a Bettington boiler The following summarises these:—

		At normal load (12 000 lb evaporated per hour from and at 100)	At 30 % Overload.
Water evaporated from and at 100° C	Total	12,300 lb	16,314 lb
	Per lb coal	9·15 ,,	9·53 ,,
Boiler efficiency		76·9 %	80·0 %

The boiler was not credited with heating the water from supply temperature (12° C) to feed-water tank temperatures (which averaged for normal load 41°, and for 30 % overload 55), nor was it debited with the power for the pulveriser, 29 E H P., which, assuming 15 lb. steam per K W, corresponds to 3 % of the steam raised

In the shops of the Missouri, Kansas, and Texas Railway, at Parsons, Kans, eight 250 h p boilers (water tube) working on coal dust, gave an evaporation per lb of combustible of 10 7 lb of water from and at 212° F The flue gases showed the high carbon dioxide content of 16%.

Coke for Steam Raising

The utilisation of coke for steam raising has, in view of increased difficulty in obtaining coal at reasonable prices, received increased attention Although coke-breeze has long been burnt satisfactorily at coke-ovens and gas works, almost entirely in hand-fired furnaces, its combustion in large power plants, with mechanical stoking, is a recent development necessitated by changed conditions. Results are so promising that more than one large electric generating station is arranging to adopt this fuel on a considerable scale.

War conditions have made coal dear and scarce, whilst coke has been little affected in price, and with increased carbonisation there has been a greater production; these factors have necessarily directed the attention of engineers to its advantages. From the point of view of fuel economy the solution of the problem of using ordinary gas works coke, suitably sized, is of great importance in connection with large schemes which are in contemplation where coal will be carbonised first, and so the valuable by-products recovered and it is not going too far to say that such schemes are largely dependent for success upon the utilisation of the coke as a steam-raising fuel. From the point of view of transport and distribution the advantage of handling one lot of coal for the gas works, which can pass on its coke to the power plant is evident. A further advantage of coke is smokeless combustion.

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[21] J., 1917, 114

Advantages are naturally set off by certain disadvantages. The average ash content is high, and frequently the moisture is excessive. The method of quenching the hot coke with water leaves much to be desired. The draught suited to coal is insufficient for coke, but with ordinary hand firing the grate introduced by the London Coke Sales Committee has proved highly efficient and not costly to instal. Steam is introduced beneath the grate and gives an impelled draught. About 3% of the steam output is required, but the steam has the further advantage of keeping the grate cool, doubtless the water-gas reaction, which is strongly endothermic, plays an important part in the combustion. The above Committee has also made arrangements for the supply of properly graded coke, the standards being: 0–$\frac{3}{8}$ in., $\frac{3}{8}$–$\frac{3}{4}$ in., $\frac{3}{4}$–2 in.

Many of the factors in relation to the combustion of coke require further working out. The most evident are the size best suited to different grates and draught conditions, the surface exposed to oxidation, the hardness and porosity all will have direct effect on the rate of combustion. Some cokes have a hard and highly glazed surface, others are dull, with surface covered with what is presumably amorphous carbon. One experienced engineer informs the writer that the latter kind is far easier to ignite and burn.

Whilst practical considerations have determined that coke is applied to existing boilers consideration of the fact that a high proportion of the fuel is burnt in the grate, the heating being largely due to radiation, points to different relationships in area between the furnace heating surface and the tube surface being required, if the best results are to be obtained. One authority states that with direct radiation from coke one square foot of heating surface will give five times the evaporation as the same area in tube surface. Closely connected with this is the fact that with economisers there is considerably less saving when coke is burnt than when coal is the fuel. This is partly due to higher localisation of the heat in the boiler and partly to the smaller quantity of excess air demanded for coke.

One fallacy in relation to the combustion of coke is that little or, as one writer states, no secondary air is required above the grate. Reference to the results obtained in the experiments by the U.S. Bureau of Mines on combustion in a hand-fired furnace (see p. 20) refutes this assumption. It was shown that with coke as well as other fuels, the furnace acted as a gas producer, and that at the surface and 1½ in. above the surface of the fuel bed a high percentage of combustible gases (mainly carbon monoxide with coke) were present. Thus with a 6-in. fuel bed and rates of combustion per hour ranging from 17·1 lb. to 79·1 lb., and air supply through the fuel bed ranging from 138 to 740 lb., the combustible gases at the surface averaged 11·8% of the total gas; 1½ inches above the surface the average was slightly higher. With 12-inch fuel bed at the surface the combustible gases averaged 23%, 1½ inches above the surface, 18%. Calculated on the data in the paper, it appears that no matter how much air is supplied through the grate, this will amount to close upon 82% of the *theoretical* air required per lb. of combustible.

In using ordinary broken coke with chain grate stokers the principal difficulties are to obtain sufficiently rapid ignition and sufficient consumption per unit area of grate to maintain the steam output. It is claimed that the average of 37 lb. per sq. ft. of grate area can be obtained, but reference to published results indicates that this is practically a top figure for coke-breeze, the smaller size of which is more favourable to rapid combustion. Ignition on the moving grate is dependent largely on the design of the brick arch. In one installation with water-tube boilers with a grate area of approximately 120 sq. ft. and a ratio of heating surface to grate area of 36·5:1, a counter-flow arrangement for the gases rising from the front section of the grate has been made, so that the arch at this point is maintained at as high a temperature as possible.

Average figures for the composition and calorific value of coke produced by one large London company are: Moisture 8·5%, volatile hydrocarbons &c. 5·0%, fixed carbon 72·0%, ash 14·5%, calorific value 10,530 B.Th.U. per lb.

COAL SAMPLING FOR ANALYSIS.

The importance of obtaining a fair representative sample for analysis cannot be over-emphasised, but the difficulty of doing so with large consignments is great. With the more general introduction of purchase based on rational lines of composition and calorific value, the matter of fair sampling is assuming greater importance. These methods of purchase are much more common in the United States than in this country, and the Bureau of Mines has issued a special Bulletin (No. 116, 1916) on the subject.

For large cargoes of 5000 tons and over it is recommended that some 3000 lb. 1000 lb. should be drawn and sampled in seven stages. First the whole should be crushed on iron plates or a concrete or stone floor to 1-in. size, piled in a cone with a workman passing round the heap and throwing the coal regularly to the top. The pile is then to be spread into a long heap by throwing out to right and left alternately. This heap is halved into two cones, one being rejected. When about 500 lb. has been obtained it should be crushed to $\frac{3}{4}$ in., halved again, and 250 lb. crushed to $\frac{1}{2}$ in. This is made into a flattened cone, quartered, and opposite quarters rejected, as usual. In the fourth, fifth, and sixth stages the sample (with quartering at each stage) is reduced to $\frac{3}{8}$ in., $\frac{1}{4}$ in., $\frac{3}{16}$ in. respectively. The sample is then thoroughly mixed and further halved until finally samples of 5 lb. each are obtained; these are placed in airtight containers, which should be completely filled. For the moisture determination it would obviously be unfair to take the sample after all this exposure. From the first "cone" (1-in. size) 1-lb. lots are taken with a scoop until the 30 lb. 50 lb. required for the moisture test are obtained. For bituminous coal a variation of 2% B.Th.U. is allowed before making any correction on the purchase price.

LIQUID FUEL.

Attention has been more specifically directed to the fuels used in internal combustion engines, particularly to the use of tar oils as substitutes for petroleum oils in Diesel engines.

As a steam-raising fuel oil has played a great part in connection with the navy, and for furnace heating in the production of shells and other munitions oil has also been an important factor, but necessarily difficulties of supply of suitable oils have been encountered. The conditions for the successful combustion of oil fuel for steam raising were dealt with at length by the writer.[22]

Lieut. L. R. Ford, of the U.S. Navy, has described[23] a form of "diffuser cone" for use with oil fuel burning from a pressure atomiser of the usual type with natural draught. The diffuser cone has an angle of 90°, and is adjustable on the atomiser. The diffuser cone is arranged inside another truncated cone, the apex of which is towards the furnace, and by means of helical vanes fixed at the base of this larger cone the air is supplied with a whirling motion between the inner and outer cone. With this arrangement it was found possible to vary the oil pressure (which quickly and closely regulated the steam production) over wide limits without smoke. Steam to meet normal requirements could be generated with spraying pressures of 50 lb. to 100 lb.

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[22] *J. Inst. Petrol. Tech.*, 1917, **3**, 19[illegible]; *J.*, 1917, 703.

[23] See *Engineer*, 1916, **122**, 286.

TAR OILS FOR DIESEL ENGINES

Many Diesel engine sets are in use throughout the country in small sized electric generating stations, pumping plants, &c., and the shortage of petroleum oils has led to extended use of tar oils. As these oils are native products and produced in large quantities, the development of their use for power production is a matter of national importance. The behaviour in practice, and the chemical and physical characteristics of oils most suited to the purpose are therefore of considerable importance both to chemists, producers, and users.

In general with tar oils it has been usual to employ a certain proportion of "ignition" oil, a petroleum product, but in some instances engines have been successfully run on tar oils alone. The ignition point of oils is one of their most important characteristics, and a valuable contribution has been made by H. Moore on "Spontaneous Ignition Temperatures of Liquid Fuels for Internal Combustion Engines."[24] Moore found the following ignition temperatures (Cent.) for the fuels in oxygen: Petrol 270°–279°; kerosenes, 251°–253°; crude petroleums, 254°–275°; gas tars, about 115°–165°; coke-oven tars, 186°–195°; low temperature tar, 307°. Considerably higher values were found for ignition in air. Petrol averaged about 100° higher than with oxygen; two kerosenes 142° and 180.5°; for crude petroleums the average was 118°. For two shale oils the difference was much less, 71° and 80°. Turpentine was exceptional, having the same ignition point in oxygen as in air (275°).

Particular interest attaches to the comparative figures for petrol, benzol, and alcohol; in oxygen they were: Petrol (aver.) 273°, benzene (100%), 566°; alcohol (sp. gr. 0.817) 395°. (in air 518°). It is well-known that a much higher thermal efficiency can be obtained with alcohol than with petrol because of the much higher compression which can be used without danger of pre-ignition, but although somewhat higher compression (with corresponding increased efficiency) is possible with benzol, it is very questionable whether anything like as high a compression as that suggested by the high ignition point found for this fuel could be safely attained.

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[24] *J.*, 1917, 109–112.

The use of tar oil in Diesel engines was very fully dealt with by Porter before the Diesel Engine Users' Association,[25] and valuable data given in the paper and discussion. Specifications for the oils are not altogether satisfactory at present. The well-known "M.A.N." Co. state that the oil should flow freely at 16° C., when cooled to 8°, and left undisturbed no separation of solid should take place within 30 minutes; ash should not exceed 0·05 %, sulphur 1 %, and the material insoluble in xylol, 0·2 %. Another continental specification includes water, not to exceed 1 %, coke residue 3 %, and 60 % should distil up to 300° C. The open flash test should not be below 62° C. (143·6° F.), or the net calorific value below 15,840 B.Th.U.

Considerable trouble was recorded as met with in separation of solids at low temperatures, and some clause in any specification should deal with this. Viscosity at selected temperatures is also a matter for consideration.

The effect of carbon in the fuel showed that there was considerable difference of opinion; one firm's experience was that engines could be run satisfactorily with as high as 8 %. It was pointed out by E. A. Evans that probably the amount was not of so much importance as the character, whether coarse, colloidal, &c. Ash in any quantity would act as an abrasive, and possibly cause choking of valves. If the coking residue is high the oil is likely to give carbonising on the top of the piston and on exhaust valves.

To overcome troubles due to separation of nahpthalene in cold weather, P. H. Smith suggested that exhaust gases might be led to chambers round supply tanks, or hot water from the cylinder jackets circulated around. It had been found that the addition of 25 % of crude petroleum oil had entirely prevented separation. In this connection the patent of Arnold Philip,[26] according to which 8 % of naphthalene is added to increase the fluidity of thick petroleum fuel oils, is of interest.

The demand for a clean tar oil, meeting in every way the requirements of internal combustion engines of the Diesel type, already exists, and will become an increasing demand, and chemists and producers should consider carefully the requirements and how the demand can be profitably met.

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[25] J., 1917, 919.

[26] Eng. Pat. 14778, 1913; J., 1914, 824.

In operating Diesel engines with tar oils with or without pilot jet ignition, it is necessary to advance the fuel admission owing to slower burning than with petroleum. With the engine load 75 and upwards tar oil can be used alone, i.e. without petroleum ignition oil, which is only required for starting. Pilot jet ignition however, enables the engine to work steadily at lower loads, and further such tar oils as are not good enough for use alone without ignition gear may be successfully used; this considerably extends the choice of oil. Compression at "no load" should not be less than 480 lb. per sq. in., otherwise ignition is uncertain, and even if ignition is regular combustion may be incomplete, leading to smoke and high exhaust temperatures. By increasing the oil injection pressure by about 20 lb. the engine runs "sweeter."

Success with any oil, and more particularly tar oil, is very largely dependent on the pulveriser. Trouble is frequently experienced with choking of the holes and passages in the fuel valve casing. All tar oils do not give this trouble, and in many cases it has been overcome by adopting another pattern of pulveriser. Naphthalene has been suggested as the cause, but there is little ground for this. The facts that another pulveriser is sometimes a cure, and, as mentioned by Porter, that the trouble is less in summer when the oil would be more fluid, rather suggest that it is due to poor atomisation. The period between cleaning out the deposit can be considerably extended, according to W. A. Turnbull, by running for a short time on a crude oil (petroleum), or paraffin, every 75 hours.

Very variable figures were quoted for the quantity of petroleum ignition oil required. Apparently under good running conditions at full load on a good engine about 8 is a fair figure. The following figures were given for various loads: 50-59 load, 15 oil; 60-69 % load, 13.9 oil; 70-79 load, 13.3 oil. From a curve the ignition oil at full load would appear to be 10.3 of the total fuel.

For total fuel oil (tar oil and pilot jet oil) consumptions per kilowatt hour the following figures were quoted: Load 31.5 %, oil 1.64 lb.; load 42 %, oil 1.02 lb.; load 67.5%, oil 0.70 lb.; load 71 %, oil 0.66 lb. The Diesel engines at Aylesbury, W. A. Turnbull stated, in a period of nine months generated 369,346 units on a consumption of 75,248 lb. of residual petroleum oil and 191,000 lb. of tar oil. This corresponds to 0·73 lb. of total fuel oil per unit as against 0.69 lb. with crude (petroleum) oil. On test runs the consumption per unit at full load was 0·735 lb. of tar oil per unit, compared with 0·65 lb. of crude (petroleum) oil.

MOTOR SPIRIT

Important "technical papers" have been published by the U.S. Bureau of Mines on "The Physical and Chemical Properties of Gasolines sold throughout the United States in 1915"[27] and on the "Properties, Laboratory Methods of Testing and Practical Specifications"[28] In connection with the last-named mention should be made of the exhaustive examination of methods employed in the analytical distillation of petroleum carried out by the U.S. Bureau of Mines,[29] with the thoroughness which is characteristic of these laboratories Reference only to this latter contribution to the literature on petroleum is permissible here, as it is hardly within the scope of the subject dealt with

In dealing with the chemical and physical properties of petrols it is pointed out that three classes were being marketed the "straight" petrol, obtained directly from crude oil, blends of "straight" petrol with "casing head" spirit, *i.e.*, the very volatile spirits which are obtained by condensation from suitable natural gas, and which are said to represent 10% of the total output, and blends with "cracked" spirits.

Very exhaustive examinations were carried out of a large number of commercial petrols The specific gravity ranged generally from 0·681 to 0·758 Those samples from eastern fields were lightest (0·683 0·737); from the Mid-continental, 0·707 0·711; from California, 0·725 0·749 The calorific values only differed over a range of 1·5%, being from 11,165 11,315 calories Sulphur was invariably low, 0·01 to 0·05%.

On distillation cracked spirits, or blends containing them, did not show any distinguishing features, but for blended "casing head" spirits the amount of distillate at low temperatures was generally much higher than for "straight" petrol, and the distillation curve, plotting volume against temperature, was much more uniform than for straight petrol.

Particular interest attaches to the quantity of unsaturated hydrocarbons present. Details are given for the methods of determining by iodine absorption (Hunt's modification of Hanus' method) and sulphuric acid. The iodine value for "straight" petrol ranged from 0·6 to 6·5. For California spirit the range was 0·6–1·5; Mid-continental, 2·0–4·0; eastern, often 1·5. Two spirits known to be "straight" gave values respectively as high as 5·9 and 6·5. It is concluded that a spirit showing an iodine value of 8 or over probably contains "cracked" spirit, and if over 10 certainly contains the latter. Some marketable wholly cracked spirits give iodine numbers of from 20–60.

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[27] Rittman, Jacobs, and Dean, *Tech Paper* 163, 1916

[28] E. W. Dean, *Tech Paper* 166, 1917.

[29] *Bull* 125, 1916

Iodine values and sulphuric acid absorption do not follow in the same order, for whilst the iodine absorption is dependent on the number of unsaturated linkages, sulphuric acid absorption is no greater with two or three unsaturated linkages than with one. With iodine values below 6·5 the sulphuric acid absorption is negligible. "Cracked" spirits show a sulphuric acid absorption of 1–6. It is stated that the content of unsaturated compounds seems to cause the users no inconvenience. No mention is made of the troublesome "gumming," due to polymerisation, which is generally found with "cracked" spirits.

From engine tests some important practical conclusions are reached. All petrols can, under properly regulated engine conditions, be made to develop the same power. If the user takes suitable care he can get almost as good results out of a cheap petrol as out of an expensive "high test" product, and the chief element of advantage of the latter petrols is that they yield maximum efficiency over a wider range of engine conditions.

In the second paper (No. 166) the desirable properties of petrol are set forth as: Not too large a percentage of highly volatile products, because of large evaporation losses and excessive danger in handling and storing, but sufficient must be present to permit easy starting; the percentage of heavier spirits must not be too high, so that after atomisation into the cylinder the heavier fractions cannot be completely vaporised or burned; there should be nothing leaving a residue, no non-combustible such as water, &c.; should be free from anything which attacks metal before or after combustion; and there should be no objectionable odour in the spirit or products of combustion.

In any specification it is deemed inadvisable to state definite limits for volatility, but the following is suggested as a good guide: (*a*) the temperature when 20% has distilled should not be below 70° C., nor above whatever limit is fixed after due consideration of the conditions of use; (*b*) the temperature when 90% has distilled shall not be above another limit similarly chosen; (c) the temperature read when 50% has distilled shall not be higher than half-way between the 20% and 90% limit (to prevent the marketing of "freak" spirits which might be unsatisfactory); (d) the dry point shall not exceed the final 90% reading by more than 55° C. This point is liberally fixed, but is intended to discriminate against improperly distilled petrols and unsatisfactory blends of petrols and kerosenes.

J. H. Coste[30] has determined the solidification points of petrol and of acetone using eureka copper thermojunctions. Petrol solidified at −128° C., acetone at −95° C. The flash-point of petrols ranged from −11 to −30° C.; for acetone, −9·5° C.

The use of coal gas as a petrol substitute is dealt with on page 63.

GASEOUS FUEL.

In an investigation of practical "Operating Details of Gas Producers," undertaken by the U.S. Bureau of Mines,[31] data sheets of enquiries were sent out to owners of producer plants and returns of a positive character obtained for 30 installations; these sheets asked for very detailed information as to costs, character of fuel, consumption per h.p. and for given section of fuel bed, depth of fuel bed, composition and calorific value of the gas, and complete data on operating. As would be expected, many returns were very incomplete, but valuable information was collected, which, although perhaps not strictly applicable to practice in this country, is sufficiently important to refer to at some length.

One great argument in favour of gas plants has been their suitability for use with inferior grades of fuel. The striking fact, however, in this report is that on the whole, the grade of fuel has been steadily improving. This is due to labour costs which are much reduced with better fuel and more than counterbalance in many cases, the extra fuel cost. Thus one coal producing company markets its coal and uses anthracite at 11 dols. because the cost of operating with bituminous coal if charged at 8 dols. is considerably more than the cost with anthracite.

The comparative fuel consumptions with different fuels are given in the following tables. Too much stress must not be laid on the values per square foot of fuel-bed area per hour, but from the operating figures supplied, together with personal observation, they were regarded as fairly representative of good commercial practice in the United States.

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[30] *Analyst*, 1917, **42**, 168; *J.*, 1917, 557.

[31] *Bull.* 109, 1916.

The rate of fuel consumption per square foot of fuel bed varies radically with different types of plant, and has led to much difference in designing and rating. In general in the United States the rate does not average much more than half the consumption originally guaranteed by early manufacturers.

Average fuel consumption in lb. per B.H.P. hour (Maximum and minimum indicated by [illegible] and [illegible].)

	Anthracite		Bituminous Coal		Lignite		Peat	Wood
U.S. Bureau of Mines			1.3	0.[illegible] 0.5	2.9	0.8 0.5	2.6	
Commercial plants	1.3	0.2 0.0	1.4	1.0 0.1	2.5	0.5 0.5		3.3

Average consumption of fuel per sq. foot of fuel bed area per hour in good general practice. (Maximum indicated by ( ).)

Type of Producer	Anthracite	Bituminous Coal	Lignite	Peat	Wood
Up draught					
Fuel as fired	10.0 (14.0)	8.5 (15.0)	12.0 (15.0)	15.0	14.0
Fuel, dry	9.0 (13.0)	8.0 (15.0)	8.5 (13.0)	12.0	
Down draught					
Fuel as fired		17.5 (26.0)	26.5 (35.0)	35.5	
Fuel, dry		16.5 (25.5)	18.5 (23.5)	25.5	
Double zone					
Fuel as fired		13.7 (25.0)	21.5 (26.5)		
Fuel, dry		12.5 (20.0)	15.0 (24.0)		

Replies on the working of the gas-cleaning plant showed that with up-draught producers results were almost invariably satisfactory with anthracite, bituminous coal, and lignite. With the two plants using wood (one stated as having a static scrubber and centrifugal tar extractor; no details for the other), both were reported unsatisfactory; tar was reported as clogging mains and admission valves and condensation of moisture and tar in the mains had given trouble. Trouble caused by lampblack was reported in several instances.

For the water used in vaporisers previous investigations had shown consumptions of from 0·7 to 1 lb. per lb. of fuel fired for up-draught producers with anthracite. An average for 20 producers on bituminous coals showed 0·7 lb. per lb. of coal. With peat containing 25%-30% water no steam was required, and in one lignite plant the water in the fuel was more than sufficient. In the Bureau of Mines down-draught producer working bituminous fuel the vaporiser consumption was as low as 0·23 lb.

In the scrubbers the water consumption naturally varied widely. On an average for seven plants working on bituminous fuel the water per lb. of fuel gasified was 64 lb. Since the make of gas may be taken as approximately 64 cub. ft. per lb. of fuel, 1 lb. of water was required per cub. ft. of gas, or 16 cub. ft. water (100 gals.) per 1000 cub. ft. of gas scrubbed.

With regard to auxiliary power actually used in operating the plants, this with up-draught producers averaged 2·8%; with down-draught 3·8%, but the latter includes one exceptionally high figure of 10%; eliminating this, the consumption is practically the same as for up-draught plants.

METAL MELTING.

With the enormous demand for alloys brought about by the war, the question of the best types of furnace and fuel consumptions has been a matter of the greatest importance, and a number of valuable papers on these questions have been published. At the Annual Meeting of the Institute of Metals several papers were read, and will be referred to here, more particularly in relation to fuel consumption and the relative merits of coke, oil, and gas for the purpose. It is noteworthy that there has been a great increase in favour of coal gas for all kinds of melting operations, but its use is not confined to melting. Large steel annealing furnaces, other smaller ones for the heat treatment of tool steels and the alloy steels for helmets are largely used; wire is annealed by gas at a consumption of some 2000 cub. ft. per ton, and gas finds another application in heating shells for "nosing." Sir Robert Hadfield has stated that his firm had used about 500,000,000 cub. ft. of coal gas in their steel works. In some large industrial towns in the north of England the gas consumption for industrial purposes has more than doubled.

In a paper on "Gas Furnaces, their Design and Manipulation,"[32] A. Forshaw said that the crucible melting furnace had made great strides in recent years, and in the last four or five years noticeably with coal gas as fuel, but the great bulk of metal is still melted with coke. The best pit type of furnace has a thermal efficiency of about 5%. The fuel consumption as a percentage of metal melted is about 30%, *i.e.*, 6 cwt.–7 cwt. per ton of brass. Often in the original square type the percentage was as high as 150. In the old large chamber type of furnace with four to six pots buried in coke, the fuel consumption rose to 300%, whilst much of the metal being in contact with the fuel and exposed to the gases, was of poor quality, containing much oxide and sulphide. Coke tilting-furnaces have an efficiency of about 15%, so that the fuel consumption in them is only about one third of that in the pit type.

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[32] Manchester Junior District Gas Association, Nov. 3rd, 1917; *J.*, 1917, 1264.

The author emphasised the difference in fuel consumptions obtained in laboratory tests and everyday foundry practice. In the former the life of crucibles and linings is not in question. In the latter there is possible inexperience of workmen, or a charge may be melted but moulds may not be ready in sufficient number, so the metal has to be kept hot; men may knock off for meals irrespective of the operations, and excessively high temperatures for the metal may be attained. Then the character of the charge, whether ingots of alloy, whether the alloy is made from ingots of the constituent metals, the proportion and character of scrap, all have important influence on fuel consumption. The following table of "practical" figures with gas is given.

Operation	Size and Type of Crucible.	Average cub. ft. Gas per lb of Metal	Average time of Melt in Minutes.[35]	
			Gross.	Net.
Melting common brass ingots and scrap (60 Cu 40 Zn)	60 lb. (pit)	2·40	35½	25
Making gun-metal (88 Cu, 10 Zn, 2 Sn)	100 lb. (pit)	3·37	48½	39
Making cartridge metal strips (70 Cu 30 Zn)	300 lb. (tilter)	3·54	72	50
Ditto ditto	600 lb. (tilter)	3·00	93	81
Making cupro nickel strips (80 Cu/20 Ni)	60 lb. (pit)	8·50	59	53
Melting aluminium	600 lb. (tilter)	3·20	49	34

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[35] The difference between the gross and net melting time represents pouring and charging, and will vary in different foundries according to the rate at which the moulds can be filled.

The following figures are given for annealing

Operation.	Load	Duration.	Cub. ft. per Ton.
	Tons	Hours	
Annealing high speed steel	3½	8	3000
Annealing steel	3½	15½	6000
Annealing cast iron parts packed in filings in boxes	0.89	3	3360

In the series of papers before the Institute of Metals dealing with "Fuel Economy Possibilities in Brass-Melting Furnaces," L. C. Harvey[34] concludes that at least one-third of this alloy is melted in tilting furnaces, the efficiency of which on coke firing is about 15. There is, however, little to choose in efficiency with this type of furnace when using coal, coke, oil, town gas, or producer gas, if the most economical size and type is taken for each fuel. With pit furnaces there is a marked difference, and those fired with town gas have the advantage.

For output and cost of melting the tilting furnace plant is a long way ahead of pit furnaces, but it has not been definitely proved that the quality of the alloy produced is the best. Many experts consider that the alloy from small pots is better. In tilting furnaces and multiple crucible pit furnaces working on town gas, 2700 B.Th.U. is required per lb. of brass.

Thornton and Hartley[35] state that coal gas is considerably more costly in terms of B.Th.U. than coke, so it must prove of much higher thermal efficiency in practice to be a competitor. A marked saving of fuel is obtained by pre-heating the metal. Data obtained without pre-heating, with only pre-heating the metal, and with pre-heating of both the metal and air appear to indicate that some advantage results in pre-heating the air other than that accruing from the mere transference of the thermal energy from the flue back to the melting chamber. This appears to be due to the higher temperature attained in the combustion zone of the furnace.

There is great advantage in being able to pack the metal closely in the pots; thus sheet scrap requires much more heat than heavy metal (see Table of Fuel Consumptions, p. 37).

G. H. Brook[36] dealt with alloys requiring high temperatures for melting, such as the copper-nickel alloy used for bullet sheaths. Tests on a commercial scale were run on a coke-fired and a gas-fired pit furnace for 10 hours on 10 days, when the following fuel costs per ton of metal were obtained: Coke (high grade metallurgical), 36·1; gas, at Sheffield rates, 31·9; gas, at preferential power rates, 24·2. No difficulty was experienced in obtaining a temperature of 1100° C. The greatest saving was in time; a weight of metal melted in 82 minutes with coke could be melted with gas in 52 minutes, and on a commercial scale 12 heats could be obtained in a working day of 10 hours with gas, whilst only on exceptional days could 7 heats be obtained with coke.

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[34] J., 1917, 1051.
[35] J., 1917, 323.
[36] J., 1917, 322.

It is well known that coal gas has superseded coke, after extensive trials of various systems, including oil, at the Royal Mint. Gas firing was introduced in 1911, the system being a low-pressure one, and the results recorded by W. J. Hocking[57] show the change to have been fully justified. Further, they are of great value because of the large quantity of metal melted and the systematic data of costs which have been kept. In the five-year period, 1905–1909, 1833 tons of all alloys, in a similar period 1911–16, 9899 tons were melted. Taking figures over these periods the fuel costs were not greatly reduced, but the cost of crucibles and labour were both very materially reduced. The following gives a comparison on one year's working:—

Year	Fuel	Metal Melted	Rate of Cost per Ton melted			
			Fuel	Crucibles &c.	Wages	Total
		Tons	s.	s.	s.	s.
1909	Coke	1198	24·3	12·4	45·7	82·4
1913	Gas	1958	22·1	26·7	10·8	59·6

The results furnish valuable data for a thermal comparison of coke and gas. Over the respective quinquennial periods mentioned the coke per lb. of metal amounted to 0·5525 lb., the gas to 5·4 cub. ft. Good quality coke should have a calorific value of 12,000 B.Th.U. per lb., and for a fair comparison the *gross* calorific value of London gas should be taken, 550 B.Th.U. per cub. ft. On this basis the relative B.Th.U. per lb. of metal is: Coke, 6650 B.Th.U.; coal gas, 3250 B.Th.U.

In order to bring the values in the different papers to a common basis for comparison, the results in the table below have been collected; those for the Royal Mint are calculated on a *net* calorific value of 510 B.Th.U. as an average for London gas. The *net* value is taken as corresponding figures by Thornton and Hartley are on this basis. The *gross* values would be about 16% higher.

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[57] *J.*, 1917, 322.

Coal Gas Consumption for Metal Melting

Metal	Pouring Temp °C.	Average No. of Melts	Per lb. Metal.	
			Cub. ft	B.Th.U. (*net*)
Yellow brass	1000	12	1·92	1031
(Cu, 70·57, Zn, 24·77, Pb, 2·99,	1000	6	2·25	1202
Sn, 1·34)				
	1000	3	2·93	1573
Red brass	1000	3	3·56	1898
(Cu, 87·4, Zn, 9·85, Sn, 2·52)	1090			
Copper (scrap sheet)	1220	4	4·98	2568
,, (ingot, 97 per cent., scrap, 3 per cent.)	1220	4	4·31	2252
,,	1220	7	3·49	1820
Gold	1150	Daily meltings	3·12	1590
Silver	1090		5·37	2740
Bronze	1165		6·50	3320
Copper-nickel	1300		9·83	5020

Figures for brasses and copper, Thornton and Hartley. Net calorific value of the gas, 515–510 B.Th.U. (*net*). Charges, 60–68 lb.

Other figures are for Royal Mint meltings by W. J. Hocking for coinage alloys, B.Th.U. per lb. metal being calculated on a *net* B.Th.U. 510 as an average figure for London gas.

H. S. Primrose[38] described a simple crude oil furnace for brass melting in 100 lb. and 200 lb. pots. With high pressure burners (25 lb. per sq. in.) the cutting action on the furnace lining and pot so reduced the life that it was not economical on the whole, although the fuel consumption was lower. Low-pressure burners, the air blast being supplied by high speed electric fans at 12 oz. pressure (20–22 in. water), were preferable. Thirty-five minutes is required to melt and pour 100 lb. brass, and 50–55 minutes for 200 lb.

The consumption of oil per 100 lb. metal melted with high pressure burners was 1·5 galls.; with low pressures, slightly over 2 galls. Assuming a density for the fuel oil of 0·9, and a calorific value (*gross*) of 19,400 B.Th.U., the B.Th.U. per lb. of brass melted at high pressures is 2620 B.Th.U.; at low pressure, 3500 B.Th.U.

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[38] J., 1917, 323.

GAS FOR STEAM RAISING.

In a paper on "Gas Fired Boilers," T. M. Hunter, before the Institution of Electrical Engineers,[39] said that generally the efficiency of gas fired boilers has been low, and the theory gained ground that gaseous fuel was unsuitable for boiler firing, and that it was impossible to obtain anything like the efficiency or the evaporation obtainable in the same type of boiler by coal firing. In view of the very important question of the pre-gasification of raw coal with a view to recovery of by-products, the coke and possibly the gas also being used for steam production, Hunter's conclusions are of considerable interest. He states that in no case yet has gas firing of boilers with by-product producer gas been made a commercial success, as it has been found that steam could be raised more cheaply from the coal direct, even after allowing for all the income from the sale of the by-products. He firmly believes, however, that there are modern producer and boiler plants even now on the market which can make the gasification and gas firing a commercial success under suitable conditions, and in the paper the important considerations on which success is dependent are considered.

Coke-oven gas gives higher efficiencies owing to the greater ease with which it can be burned, and is particularly suitable for firing water-tube boilers. With suitable combustion arrangements evaporations of 5½ lb. per sq. ft. of heating surface can be obtained at the highest efficiency.

Blast furnace gas, provided it is clean and supplied under suitable pressures, gives good results in both Lancashire and water-tube boilers. In the former evaporations of over 8000 lb. per hour can be obtained; with the latter from 5 to 5½ lb. per sq. ft. of heating surface. With Lancashire boilers the author had experience of regular evaporations of 9000 lb. per hour from ordinary 30 ft. by 8 ft. boilers, or nearly 10 lb. per sq. ft. of heating surface, which "corresponds very closely to the evaporation per sq. ft. claimed for the Bonecourt boiler at the lower sections." A disadvantage of the Lancashire boiler on gas is the low temperature drop in the flues, which is not sufficient to cause good water circulation.

With water-tube boilers about 80% of the load should be evaporated in the first bank of tubes; 15% in the second; and 5% in the third. The low maximum evaporation of 5 to 5½ lb. per sq. ft. of heating surface with gas is thus accounted for. It is important that sufficient combustion space should be provided for the large volumes of gas to be burned, so that combustion may be completed before passing through the tubes. External combustion chambers cause unnecessary heat losses by radiation and conduction, and because the highest temperature is not attained in the immediate vicinity of the tubes. The usual method of gas firing of admitting the burning gas through an opening near the door and the air by the door is undoubtedly crude, yet, as the author points out, more boilers are fitted with this arrangement than with all other arrangements put together.

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[39] See *Engineering*, 1917, **104**, 613; *J.*, 1918, 45A

The maximum flame temperature should be found in the region of the boiler within a few feet of the burner, and there should be a minimum volume of flue gases carrying away heat to the chimney. When a short intense flame is required either air or gas must be under considerable pressure. With the whole of the air supplied to a proper mixing arrangement no secondary air need be used and the author believes that by this method, which puts the furnace under pressure, and by simply drawing off the products of combustion by the chimney draught, there would be considerable advances in boiler output combined with high efficiency. Experiments in America with water-tube boilers show that a smaller combustion space is needed in proportion as the air and gas are more intimately mixed in the burners.

Combustion arrangements where there is a steady pressure of gas are usually of the Bunsen burner type, but the burners must often consume from 80,000 to 100,000 cub. ft. of gas per hour, and a good burner provides its primary air, about 60% of the total air for combustion. With intermittent gas pressures (as with many blast furnace plants) a type of burner on the injector principle has recently been developed. The mixing tube is conical, expanding in cross section from the gas inlet to the burner nozzle. The burners are so proportioned that the speed of the mixture of air and gas is greater than the speed of the explosive reaction of the mixture, and with suitable pressure combustion takes place at the end of the cone. When the gas pressure falls the gas burns at that point where the speed of the gas-air mixture corresponds to the backward speed of the flame. When gas fails (as with lowering of the bell) the flame is extinguished, re-ignition being ensured by a small coal fire under the burner. This burner automatically adjusts, over considerable variations of pressure, the weight of primary air drawn in to the weight of the gas passing.

J. B. C. Kershaw[40] gives results obtained with coke-oven gas by

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[40] *Engineer*, 1917, 124, 28.

Balow and Dobblestein using the Terbeck burner, which ensures good mixture and is provided with safety devices to prevent back firing. In each case double fire flue boilers were employed.

	Terbeck burner	Wefer burner
Sq. ft. heating surface	1280	1241
Mean calorific value of gas, B.Th.U. per cub. ft.	465	428
Excess air supply	1·71	1·16
Evaporation per 1000 cub. ft. gas	286·5 lb.	291 lb.
Evaporation per sq. ft. of heating surface per hour	4·47 lb.	5·81 lb.
Thermal efficiency (to saturated steam)	71	77·6
Thermal efficiency with superheat . .	79·2	81·6

Coal Gas as a Petrol Substitute

One of the most striking developments in the use of coal gas has been its wide and successful adaptation as an emergency fuel to meet the requirements arising from the great shortage of petrol. The usual special gas bags are unsightly, and special provision has to be made for carrying them; with small cars this necessitates a "trailer." If the gas could be carried at high pressures in steel cylinders certain advantages would arise, but there would be compensating disadvantages in weight, in a very limited number of stations provided with the necessary compression plant, and in the cost of compression, besides a possible element of danger in the event of an accident. A compromise between the two extremes may be found in the proposition to use a container made on the lines of the pneumatic tyre; it is estimated that a 250 cub. ft. container with gas at 250 lb. pressure would be 7 ft. long, 15 in. diameter, and weigh 50 lb. Gas-driven tram cars have been in use at Neath for over 15 years, the gas being stored in steel cylinders.

On a gross calorific value for petrol of 141,000 B.Th.U. per gallon and for coal gas 550 B.Th.U. per cub. ft., 260 cub. ft. of gas is thermally equivalent to 1 gall. of petrol. On this basis 1000 cub. ft. of coal gas at 4*s*. would be equivalent in cost to petrol at just over 1*s*. per gallon.

Several comparative results in practice have been recorded, but are not of the nature of scientific tests. Under the best conditions it appears that 1000 cub. ft. of gas is about equivalent to from 3 to 3·5 galls. of petrol. At Great Grimsby the motor bus service has reduced running costs per mile from 4·30*d.* on petrol to 1·66*d.*, the price of the petrol being 2s. 2*d.* per gall. and the gas 2s. 6*d.* per 1000 cub. ft.

The "Commercial Motor" has published the following data on bench tests on "W. D. subsidy engines," made at the works of Messrs. Dennis Bros., Ltd., Guildford. At 1190 revs. per minute, horse power developed, on coal gas 43·5, on petrol 49·5. The gas consumption per hour was 1200 cub. ft., giving 27·6 cub. ft. of gas per h.p. hour. At 1160 revs., h.p. developed, on coal gas 40·5, on petrol 48·0. The gas consumption per hour was 1011 cub. ft., giving 25·0 cub. ft. of gas per h.p. hour.

Unfortunately petrol consumptions are not stated. Assuming however 0·7 pint per h.p. hour, the petrol consumption at 1190 revs. is 4·33 galls., and at 1160 revs. 4·2 galls., and the quantity of petrol per 1000 cub. ft. gas is approximately 3·6 and 4 galls., a figure in fair agreement with that generally found in practice on the road.

Messrs. Dennis Bros. have since furnished the writer with further particulars of tests on the two fuels with an engine having a cylinder of 115 mm. bore and 170 mm. stroke. At 1170 revs. per minute, 41·5 B.H.P. was developed with a gas consumption of 1020 cub. ft. per hour, or 24·6 cub. ft. per B.H.P. per hour. On petrol running at 1260 revs. per minute, the consumption was equivalent to 0·72 pint per B.H.P. hour.

The calorific value (*net*) of the coal gas averaged 480 B.Th.U., so that the equivalent per B.H.P. was 1120 B.Th.U. Petrols vary but little in calorific value, and assuming the *net* B.Th.U. per gall. to have been 131,500 B.Th.U., the equivalent per B.H.P. was 12,100 B.Th.U. Coal gas shows a little higher thermal efficiency, but on an average Messrs. Dennis state that the B.H.P. obtained on coal gas is about 85% of that obtained on petrol.

With a special coal gas carburettor (mixer ?) fitted to a Belsize delivery van, an average distance of 19·2 miles was run on 250 cub. ft. gas, as against 18 miles when gas was employed with the usual petrol carburettor, a result showing an improvement of nearly 7%.

IGNITION AND COMBUSTION OF GASEOUS MIXTURES.

J. W. McDavid[41] has devised a method which eliminates the time factor in the ignition of gaseous mixtures, which in most previous methods probably caused the values for ignition temperature to be too low, since sufficient time elapsed before the ignition temperature was reached for a process of slow combustion to ensue which generated sufficient heat for the remainder of the gaseous mixture to be raised to its ignition point. In the Dixon and Coward method the rate of flow of the gases also has to be taken into account.

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[41] *Chem. Soc. Trans.*, 1917, **111**, 1003; *J.*, 1917, 1264.

McDavid's method consisted in bringing a soap bubble blown with the gaseous mixture in contact with a suitably heated hot body of small dimensions. With a bubble of not more than 3·7 cm. diam. instantaneous ignition took place, with larger bubbles the mixture could be made to ignite at lower temperatures. Three types of igniter were employed, (*a*) a platinum wire (0·025 cm.) wound in coil round silica tubes; (*b*) a cylindrical piece of iron 3·75 cm. long and 1·9 cm. diam., with a flat side and a small hole drilled just beneath the surface to carry a thermo-junction (later a hole was drilled so as to expose the thermo-junction). The block was heated by a blowpipe; (*c*) a coil of platinum wire (0·025 cm.) wound on two mica strips, the whole being 3 cm. long by 0·3 cm. wide. A thermo-couple was inserted between the strips. In (*a*) and (*c*) heating was effected by means of an electric current. The last arrangement (*c*) was finally adopted, and the temperature deduced from readings of the current passing, it being found that the thermo-junction gave erratic results.

A calibration curve was obtained by plotting current against temperature, deduced from the fusing points of potassium iodide (687° C.), potassium bromide (723° C.), sodium chloride (800° C.), and potassium sulphate (1072° C.). For this range of temperature the ammeter readings ranged over 1·71, so that an error of 1 in the readings meant a temperature variation of 1° C. McDavid concluded that his results might be subject to an experimental error of ± 3°. Unfortunately no data for physical properties are so widely different as those for the melting point of salts. McDavid's temperatures are in close agreement, but not identical, with those obtained (1893) by Meyer, Riddle, and Lamb, who used a gas thermometer. More recent figures (1903) by Ruff and Plato, using a platinum/platinum-iridium thermo-junction, are:—KI, 705°; KBr, 750°, NaCl, 820°, K_2SO_4, 1050° C. McDavid's selection of temperatures may be correct, but, until there is more certainty of the actual melting points of salts, absolute figures for ignition points based on them must be accepted with some reservation.

The results obtained, however, are of considerable interest, for they are far higher than any hitherto obtained. The final values, together with those of Dixon and Coward for gases, are given in the following table. In each case the mixture was with air.

	McDavid.	Dixon and Coward.
Hydrogen (10%)	717° C.	585° C.
Methane ...	Over 1000	640 750
Ethylene	1000	543
Carbon monoxide	931	651
Petrol (boiling 40°(?)–80°)	995	
Benzene ...	1062	
Ether	1033	

The higher results certainly show that there is a great deal in the author's contention that "slow" combustion is initiated at low temperatures under the usual conditions of experiment, this preliminary stage causing rise of temperature to the real (instantaneous) ignition point. As already mentioned there may be some error in the absolute values for ignition due to uncertainty of the melting points on which the igniter was calibrated. Further, catalytic effect of the wire may be considerable, and undetermined, for with silica tubes and Eureka thermo-junctions, the results for hydrogen (20%)–air mixtures were in one case 30° lower than with platinum–platinum-rhodium thermo-junctions in identical silica tubes, and in others 23° and 21° lower, these differences being ascribed to greater catalytic effect of the Eureka wire.

R. V. Wheeler[42] has further investigated the "stepped" ignition which W. M. Thornton had observed in gaseous mixtures. Discontinuities, or "steps," were said to have been found when an impulsive electrical discharge caused ignition of a combustible gas and air when the composition was varied, the pressure being constant, and when a mixture of given composition was ignited, the pressure being varied. Thornton observed that with methane and air, ill-defined steps were noted only when the methane content was varied, the electrodes not being clean. Wheeler has been unable to detect any discontinuity in this mixture, or with hydrogen or any of the gaseous paraffin hydrocarbons and air, and concludes that Thornton's "stepped" ignition required some conditions of experiment which Wheeler was unable to reproduce.

Wheeler and Whitaker[43] have investigated the explosive limits of acetone vapour and air. The usual variations are noted with varying diameter of tube, and whether ignition is at the top or bottom, the tube being vertical, or when the tube is horizontal. Their general conclusion is that in a large tube (60 cm. or over) the lower acetone vapour limit is approximately 2%, the upper 10%. In a tube of 2.5 cm. diameter the maximum speed of flame propagation was 9.6 cm. per second, the mixture containing 5.15% acetone vapour. The theoretical percentage for complete combustion is 4.76%. It is concluded (from results for methane and air) that with larger tubes the speed measured in the 2.5 cm. tube would be multiplied by 2.5 for 30 cm. diam.; by 3 for 60 cm. diam.; by 3.5 for 90 cm. diam.

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[42] *Chem. Soc. Trans.*, 1917, **111**, 130; *J.*, 1917, 378.

[43] *Chem. Soc. Trans.*, 1917, **111**, 267; *J.*, 1917, 587.

A paper on the "Limits of Inflammability of Mixtures of Mine Gases and of Industrial Gases with Air" recorded the result of work in the U.S. Bureau of Mines Laboratories[44] by G. A. Burrell and H. W. Gauger. Burrell and Robertson have extended the observations with methane-air mixtures and investigated the effect of temperature and pressure on the limits of combustion. Near the lower limit (5.5% methane) propagation occurred at 25° C.; at 200° with 5.15%; at 300° with 4.88%; at 400° with 4.55%; at 500° with 4%, whilst with percentages slightly below each specified there was no propagation at the respective temperatures. Hence a mixture too weak to propagate ignition at ordinary temperatures does so at higher temperatures.

Most interesting results were obtained with variation of pressure. Raising the pressure up to five atmospheres did not alter the lower limit, so that a mixture too weak to ignite at ordinary pressures will not ignite on moderate compression. On the other hand, reduction of pressure had an unexpected effect in view of the above results; a mixture which would propagate ignition failed to do so if the pressure were sufficiently reduced. Starting near the lower limit (5.5% CH_4 at normal temperature and pressure), a reduction of some 200 mm. would prevent ignition; as the percentage of methane was raised, so the reduction of pressure had to be greater until nearly the theoretical methane content (9.4%) for complete combustion was attained. At this composition the maximum reduction to prevent ignition was found, the actual pressure being 275 mm. Then with further increase of methane the reduction required to prevent ignition became less and less. The curve therefore was inverted. It follows that at atmospheric temperatures no methane-air mixtures will ignite below a pressure of 275 mm., and the mixture in nearly theoretical proportions has the greatest range of ignition with changing pressure.

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[44] *Tech. Paper*, No. 150, 1917; see *J.*, 1917, 955.

FUEL ECONOMY.

The necessity for economy in the production and utilisation of coal has been a subject for serious consideration since the outbreak of the war, owing to reduction of output, difficulties of transport, and increasing demands arising through activity in production of munitions, particularly iron and steel. Several valuable papers on the subject have appeared in the Journal. Further, the large demands of the Navy for fuel-oil, the fact that practically all such oil has to be ship-borne, and the reduction of tonnage from one cause and another, have combined to emphasise the importance of home production of suitable oils, either from shale, or by destructive distillation of coal, especially low temperature distillation, and important Departments are engaged in investigating these questions.

The general effect of the economic conditions arising from the war has been to speed up investigations on important fuel questions, to an extent which, in normal times, it would have taken years of persistent advocacy to achieve.

The first sign of this awakening was the appointment of a Committee on Fuel Economy by the British Association. Later a Fuel Research Board was appointed by the Committee of the Privy Council for Scientific and Industrial Research, with the main object of making a survey and classification of the various coal seams, and investigating practical problems involved in carbonisation and gasification of coal. Full reference to the early work accomplished will be found in the first published Report.[45] Several problems are outlined and the hope is expressed that the solutions of some will be supplied by workers in the industries. The Board "would regard it as a great misfortune if the establishment of a Government organisation for Fuel Research were to result in the discouragement or limitation in any way of the activities of outside workers or organisations." To attain this co-operation, periodical reports should be issued, giving description of methods, results of investigations, &c., otherwise there is bound to be much working in the dark and unnecessary overlapping. A Fuel Research station is to be erected at East Greenwich, on land offered on very advantageous terms by the South Metropolitan Gas Company, which Company will also give facilities for the transport of coal, and take over at market prices gas, tar, liquor, coke, &c.

The Coal Conservation Committee appointed by the Ministry of Reconstruction to consider the economy which might result from the conservation of coal in the production of motive power and other forms of energy for industrial purposes, the expansion of industry which would result in the way of new manufactures from the proper use of coal, and the steps necessary to obtain these objects, has published an advanced proof of recommendations. It is suggested that Great Britain should be divided into sixteen districts with one authority in each dealing with all generation and main distribution ; suitable sites for electric generating purposes should be chosen on important waterways for each district, so that there will be ample water and transport facilities; these sites should be sufficiently large to provide for by-product recovery and for new electro-chemical industries.

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[45] J., 1917, 1074.

Plans should be prepared immediately after the war for large power plants to supply existing demands, and secondly, electrical energy at the lowest possible price for new processes and manufactures. Power available from surplus gas or waste heat should be turned into electrical energy in local plants and fed into the main distribution system. It is contemplated that, under such a scheme, coal which it does not at present pay to bring to the surface would be used economically on the spot, or where transport conditions were favourable, at the central site.

With regard to existing undertakings it is considered possible to stop extensions of uneconomical stations, mostly built on cramped or unsuitable sites, and arrange to supply them with power from the central system It is suggested that a Board of Electricity Commissioners should be appointed, with full powers to deal with the electricity supply throughout the country , with power to stop the extension or multiplication of uneconomical stations for public supply ; to standardise for each area the frequency and voltage of the main transmission and distribution system , to arrange for the handing over, on equitable terms, of existing plant, &c., in each area to a new electricity body, and to settle the conditions governing and establishing this new body.

Such a scheme as that briefly outlined is mainly on the lines of schemes which have been advocated for some time past as necessary in the interests of fuel economy, and is in large measure exemplified in the present North East Coast power system. From the point of view of chemical industry the adoption of such a scheme would be of the greatest importance. Already many applications of electricity to chemical industry, not hitherto practised in this country, are on record. H. Peile[16] states that current at one of the Newcastle stations, included in the N. E. Coast scheme, is being supplied for the production of ferrosilicon (the output from one 2000-k.w.

[16] [illegible] J., 1917, 1[illegible]2

furnace being 10–15 tons per day), ferromanganese, ferromolybdenum, ferrochromium, and ferrotungsten. The production of these alloys, so vital for steel industry, is a national matter of the highest importance. In addition from 300–400 tons of cuprous oxide (which prior to the war all came from Germany) is produced, together with some carborundum and calcium carbide.

Among other applications of electricity may be mentioned the Kilburn-Scott three-phase furnaces at Manchester for the production of nitrates from the air; a 10,000 k.w. plant at Manchester for the manufacture of calcium carbide; the production of phosphorus and Arcorundum (a body similar to carborundum) at Wolverhampton. Electric furnace plants are being rapidly extended in Sheffield; it is estimated that by the middle of the present year some 85,000 tons of steel will be produced from current supplied by the Corporation Electricity works.

These, and many other industrial applications of electricity to chemical and metallurgical processes, are in every way to be encouraged, and, if they are to compete successfully with foreign competition after the war, can be maintained only through the more economical use of waste heat and a general maximum utilisation of our fuel resources.

In connection with the strenuous advocacy of the prohibition of the use of raw coal and the utilisation of gas for power production, the expert opinion of engineers appears, on the whole, far more favourable to steam-driven turbo-generators than to gas-driven plants for large electric stations. J. A. Robertson[47] considers that there is still a large margin for improving the efficiency of the direct-fired boiler with turbo-generators by an increase in the steam pressure and superheat. With 350 lb. pressure and a steam temperature of 700° F (amounts not yet reached in practice) the thermal efficiency of boilers, economisers, electric generators and condensers is estimated at over 22 %; allowing 3 % for auxiliary power demanded, and 12 % for transmission and transformer losses, an overall efficiency of 18·8 % should be attainable for the energy delivered to the consumer. This is equivalent to a coal consumption of 1·09 lb. per e.h.p. or 1·45 lb. per k.w. sold.

It has been stated that a turbo-alternator is under construction of 100,000 h.p. (70,000 k.w.), whilst the largest reciprocating engine yet built is 25,000 h.p.

An entirely novel departure in power plant, and one which should have very considerable bearing on fuel economy, has been made at the works of the well-known Ford Motor Co., at Detroit. It consists of a parallel combination of steam and gas engines, which drive on the same shaft, and is intended to combine the economy of the gas engine under constant load, with the reliability of the steam engine under varying load. The very important feature, however, is the conservation of heat which will be effected. Between the high and low pressure cylinders of the steam engine exhaust gases from the gas engines serve to superheat the steam. Another portion of the gas engine exhaust jackets the high pressure steam cylinder, so reducing heat losses. The exhaust steam from the low pressure cylinder passes through a surface condenser and serves to heat the water for the heating pipes and radiators throughout the factory. Further, the cooling water for the gas engine cylinders becomes raised to 160°–180° F., it is then further heated to about 250° F. by the exhaust gases from the gas engines after they have passed through the steam superheater or jacket of the high pressure steam cylinder, and serves for the boiler feed-water. For the steam engines it has been estimated that 18·57 % of the heat in the steam, or 13·9 % of the heat in the coal, will appear at the switchboard as electrical energy. With the gas engines, 21 % of the heat energy in the gas, or 20·4 % of the heat energy of the coal, will be available at the switchboard. In all, 60 % of the total heat energy of the coal will probably be utilised.

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[47] See *The Engineer*, 1917, 123, 579.

GAS. DESTRUCTIVE DISTILLATION. TAR PRODUCTS.

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Town's Gas.

From early in 1917 there has been an increasing volume of discussion both inside the gas industry and out, concerning the question as to what should constitute the best all round standards in the supply of town's gas. Shortage of coal, inferior coal, toluol and benzol extraction, and the difficulty in obtaining new plant, have put many undertakings *in extremis* in that it has been practically impossible to produce enough gas of normal quality at usual pressures. Now that most of the large concerns have dispensed with the illuminating power standard, it is no longer of much consequence to note what effect these difficulties have had on the results obtained from the flat flame burner. Various authors have shown that the extraction of one gallon of crude benzol from 12,000 cubic feet of gas is to reduce the illuminating value of the gas by 2·5–3·0 candles, and the calorific value by about 13 B.Th.U's.

To increase the volume of gas produced, many undertakings have been compelled to put rather more "pull" on the retorts than is usual, and consequently, furnace gases have been mixed with the straight coal gas. This has had ill-effects all round, as not only has the gas efficiency of carbonization been reduced—fewer B.Th.U's. in the form of combustible gas being obtained from the coal—but naphthalene troubles have in many cases been increased, and the tar yield reduced. The tar has also contained a higher percentage of pitch, these latter troubles having been caused by the over-heating of the gas with hot furnace gases.

The specific gravity of the gas has considerably increased and distribution troubles have been correspondingly enhanced. The extraction of most by-products has been reduced in efficiency owing to the increased dilution of the gas.

Most gas undertakings have now adopted, for a period of years, the standard of 500 B.Th.U's. gross, but owing to the serious depreciation in the results obtained in use from the gas supplied from many undertakings, there is a tendency to insist that there should be other standards besides that for calorific value. Those responsible on both sides will do well to avoid even suggesting the multiplication of standards until much more is known upon the subject. It is of national importance that heat energy in the form of gas should be supplied at the lowest possible price, and increased restrictions can but raise the cost of production. It is almost universally agreed that even should an ideal gas be produced the questions of constancy of quality and pressure are overwhelmingly important.

A Gas Investigation Committee was appointed by the Institution of Gas Engineers early in the year. This includes the Gas Heating Research Committee of the Leeds University and the Institution which has in hand an extensive research into the results to be obtained from gases of widely different quality when used in already existing appliances.

The Board of Trade have appointed a "Fuel Research Board" with Sir George Beilby as President.

Two main lines of research are under consideration :

(1) A survey of classification of the coal seams in various mining districts by chemical and physical laboratory tests

(2) An investigation of the practical problems that must be solved if any large proportion of raw coal is to be replaced by other forms of fuel obtained by the carbonization or gasification of coal

The subject of low temperature carbonization will receive thorough consideration.

The Board have set themselves to attempt to reply to the following questions :

(1) Can the raw coal used for domestic heating (35 to 40 million tons per annum) be replaced by smokeless fuel, solid or gaseous, prepared by the carbonization of this coal ?

(2) Can adequate supplies of fuel oil for the navy be obtained from the carbonization of the coal at present used raw in the domestic grate ?

(3) Can town's gas be obtained in a more economical way than it is at present being obtained ?

(4) Can electric power be obtained more cheaply if the coal used for steam raising is first gasified or carbonized ?

(5) Can the peat deposits of the United Kingdom be utilised so as to be a serious source of fuel for industrial purposes ?

(6) Can the use of gaseous fuel be forwarded by the development of more scientific methods of combustion in furnaces, etc. ?

A Fuel Research Station is to be erected on land provided near a works owned by the South Metropolitan Gas Company.[1]

Blue Water Gas in Town's Gas.

It has been the practice in the past for many gas undertakings to make carburetted water gas and mix anything up to 25% with the coal gas, the mixture being termed town's gas. The necessary petroleum "gas oil" is now practically unobtainable owing to shortage of tonnage and its requisition as fuel-oil for the navy. Largely for this reason, and partly because the production of water gas is a means of reducing the demand for coal gas, companies have been urged by the authorities to increase their make of blue water gas, and consequently the proportion present in town's gas. There is no doubt this has proved in the main a very useful method of procedure as it has enabled gas engineers to carbonize their coal more efficiently and increase the quantity and quality of the tars a factor of utmost national importance. The calorific value of the town's gas has been somewhat reduced, but the low inert content of blue water gas, and the reduced volume of air required for combustion per B.Th.U., have tended to increase the efficiency, in use, of the mixture.

A similar end has been attained by a number of workers, notably Blundell and West, in their experiments on steaming in continuous working vertical retorts. Steam in varying quantities is passed up the retort through the incandescent coke and through coal which is undergoing carbonization, and considerable volumes of water gas are formed.

Blundell[2] states that it has been shown that there is no advantage on cost in producing water gas in the intermittent vertical retorts over the usual method of production of blue water gas. He passes steam into the retort (Glover-West continuous system) above the coke extractor, to reduce condensation. The quantity of steam used will vary with the quality of coal and its coke. It is essential that the required temperature be attained in the coke for the water gas reaction and consequently the throughput of coal was reduced by 10%, but the make of gas per ton of coal was increased from 12,000 to 15,500 cubic feet, the calorific value being reduced from 530 to 510 B.Th.U. gross. Slight "pull" was worked on the retorts. The quantity of scurf was reduced, and that found, was easier to remove.

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[1] *See J.*, 1917, 1054.

[2] *Gas J.*, 1917, **139**, 106; **140**, 213; *J.*, 1917, 860, 1172.

No destructive action was found to have taken place on the brickwork of the retorts. When using steam to the extent of 14% of the coal carbonized, it was found that the quantity of fuel used in the producer was increased by one pound per 100 lb. of coal carbonized.

By the adoption of this process on a works making 200 million cubic feet of gas per annum, Blundell claims a saving on the cost of production of the gas of 30% and 3577 tons weight of coal (approximately 20%). The increased make of gas would appear to be due to the production of water gas and the more complete distillation of the coal. In addition, the steam and water gas sweep the hydrocarbon vapours, as they are made, more quickly from the highly heated zones in the retorts, and a much smaller proportion is completely cracked to carbon and hydrogen, etc., with the consequent reduction of scurf in the retort and pitch in the tar.

About the time when gas engineers and gas consumers were showing intense concern at the difficulties caused by the production of gas of lower calorific value than has been normal, owing to the exigencies of the war, Mr. George Helps, of Nuneaton, came forward with definite proposals for, among other things, perpetuating a condition of things which had almost universally come to be considered as eminently undesirable.[2] Mr. Helps asserts that gas even as low as 350 B.Th.U. nett, will generally give as good results as gas of 500 B.Th.U. nett, foot for foot, owing to the inefficient way, due to poor aeration, in which the higher quality gas is usually consumed. He claims to have proved his case by experiment and large scale experiences. He advocates that the lower grade gas should be produced by mixing air, nitrogen, producer gas, or blue water gas with high grade coal gas before it leaves the works. He also claims higher and better tar yields, and lower cost of production. Some of his condemnations of gas of 500 B.Th.U. and of gas appliances when used with such gas, are by no means justified, but those interested would be well advised to reserve their judgment until further authentic facts and data are available. Mr. Helps will have achieved a great deal if he has only caused the gas industry to review the whole position of gas production, distribution, and use.

Steaming on Continuous Verticals.

Wellens[3] gives results of extensive tests carried out on an installation of Dempster-Toogood continuous vertical retorts. No figures are given for either the quantity of steam used nor its temperature of superheat, but 15,000 cubic feet of gas of 540 B.Th.U. gross calorific value was obtained per ton. The amount of steam was varied as conditions demanded. Unlike Blundell, he found steaming to have no effect on the formation of scurf. Wellens, however, agrees that the temperatures at the bottoms of the retorts should be highest.

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[2] *Gas World*, Dec. 29, 1917.

[3] *Gas J.*, Nov. 20, 1917.

A number of workers have substituted hot blue water gas for steam in the retorts. This appears to have all the advantages of steam without the reduction in temperature of the charge and the consequent increase in the fuel bill. The carbon dioxide in the blue water gas is also partially converted into carbon monoxide by contact with incandescent coke, but there is no production of blue water gas.

Carbonization and Complete Gasification of Coke.

Naumann[4] describes the Dellwik-Fleischer system of gas production. The plant consists of a continuously working vertical retort. The coke leaving the bottom enters a water gas generator. The " blow " gases go to the atmosphere and the hot " run " gases (blue water gas) pass up through the retort with the products of distillation. Any temperature of carbonization may be maintained by admitting either air or steam into the retort with the blue water gas. The process is known as the " Tri gas " process. Any kind of coal may be used. A typical analysis of the gas from a good coal is given—H_2 50%, CH_4 10%, CO 30%, Cn Hm 1%, CO_2 5%, N_2 4%. The calorific value ranges between 210 and 370 B.Th.U. Its flame temperature is high due to the small percentage of inert constituents and low requirements for air. It is claimed that the gas can be made at 2d. per 1000 cubic feet.

Low Temperature Carbonization.

Low temperature carbonization continues to be a subject of interesting discussion in the technical press, but unfortunately very few results of actual practice on a large scale are available, though some systematic work is in progress.

Winmill,[5] after carbonizing a " bastard cannel " in 8 cwt. charges in an iron retort for periods of 8 hours, at a temperature of 500° C., and reduced pressure of 26 in. to 28 in. of mercury, came to the conclusion that low temperature distillation of high-ash coals is not commercially economical. The tar was found as an emulsion. He obtained 6000 cubic feet of gas to the ton, and 25 lb. of sulphate of ammonia. The gas was not washed for either ammonia or light oils, and no figures are given for the quality of the gas.

Capps and Hulett[6] present results of tests of the distillation of coal under pressures in an electrically heated steel cylinder. At 600° C. and up to 20 atmospheres, the quantities of compounds of high boiling point are reduced, but the quantities of condensible vapours of low boiling point are increased. This they state is due to the "cracking" of heavy vapours within the retort. As the pressure rises the amounts of phenols and tar acids are reduced. The proportion of coke and the percentage of fixed carbon in the coke are increased with pressure owing to "cracking" effect. The calorific value of the coke is increased, but the percentage of nitrogen, oxygen, sulphur, and volatile matter was found to have decreased, probably due to the increased partial pressure of hydrogen in contact with the hot coke. At temperatures below 600° C., increase in pressure increased the volume of gas evolved. The amount of hydrogen is increased by pressure up to 20 atmospheres at 500° C. but reduced between 550° C. and 600°. The increase is probably due to "cracking," and the decrease to the action of the hydrogen on the unsaturated compounds and on the nitrogen, sulphur, and oxygen of the coke.

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[4] *Gas J.*, July 10, 1917; *see J.*, 1917, 538. [5] *J*, 1917, 912–915.

[6] *J. Ind. Eng. Chem.*, 1917, 9, 927–935; *J.*, 1917, 1229.

Whitaker and Crowell[7] have ascertained the temperatures at which the maximum formation of benzene (800° C.), toluene (700° C.), and xylene (600° C.), occur. These results agree closely with those obtained in the cracking of petroleum oils, and probably the course of the reactions is the same in both cases. If washed gas be recirculated through the retort, the period of the carbonization reactions is reduced and the yields of light and heavy oils, benzene, toluene, and xylene are increased.

Influence of Iron and Lime on the yield of Ammonia.

Hollingsworth[8] has carbonized at 800° C. coal containing the "normal" quantities of iron and lime, to which he has added 10% of either, and obtained the following results :—

—	Normal.	+ 10% of Fe_2O_3.	+ 10% CaO.
Nitrogen in coke	55·2	58·27	60·76
Nitrogen as NH_3	21·7	17·31	24·14
Nitrogen elsewhere	23·1	24·42	15·10

These results supply an extra reason for removing iron pyrites from coal.

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[7] *J. Ind. Eng. Chem.*, 1917, 9, 261-262 ; *J.*, 1917, 446.

[8] *Gas World*, March 3, 1917.

COKE DUST.

Where coke is thoroughly graded and screened about 5% to 10% of the coke made remains as dust (below ½ in.). This is mostly sent to the tip, but valuable uses are being found for it and it is rapidly becoming a marketable product.

Under special but simple conditions it is being employed on a very extensive scale in some districts as a boiler fuel. Its calorific value is equal to that of the original coke, and when used in a tubular boiler and Crossthwaite grate one pound will evaporate 4½ lb. of water, and the output of the boiler is as much as 75% of that with a good slack.

Extensive experiments are being carried out on the gasification of this material, though sulphate recovery would not be profitable. The fuel is so cheap, however, that with a low blast, wide grate, shallow fuel bed, and mechanical grate, the experiments should meet with some success. Dust is also being mixed with tar and carbonized. The tar is partially distilled and a fair coke is found as residue.[9]

During the year much work has been done in connection with the use of coke in producer practice. Sulphate recovery is not economical owing to the low available nitrogen content of the coke, and the cost of recovery plant and its operation, including the excessive amount of steam required for blast saturation. Non-recovery conditions are therefore adopted, and so long as the blast saturation is not higher than 60° C. (*i.e.* 0·5 lb. of steam per pound of fuel gasified) the gases may efficiently be used direct from the producer—if satisfactory dust catchers are employed. Unscreened coke from [illegible] in. down may be gasified in low-pressure producers with mechanical grates, and there will be no more clinker troubles than are experienced with normal producer slacks. This naturally depends much on the ash content and composition of the coke. The producer can maintain its full load, and the quantity and quality of the gas amount to an average of 120,000 cubic feet per ton of 130 B.Th.U. nett. The Tees and the Kerpely types of low-pressure producers with mechanical grates have proved quite satisfactory in this connection. The following results have recently been published.

The Woodall-Duckham installation of continuous vertical retorts installed at Tottenham is heated by means of producer gas made from coke breeze in four Tees producers having mechanical grates. One producer acts as a standby. 33 lb. of coke is used per hour per square foot of grate area. The generator efficiency is 63% on the nett. The fuel had the following grading:- 27·6% over ½ inch, 33·1% ½ inch—¼ inch, 19·3% ¼ inch—⅛ inch, 20% below ⅛ inch. The gas consists of CO_2 6·4%, CO 25%, H_2 14%, and has a nett calorific value of 124 B.Th.U. The make is 110,000 cubic feet. Blast saturation 63°C., blast pressure 18 cm., temperature of gas leaving the producers 191·5°C. The coke contains 14·29% moisture, 22·33% ash 5·1% volatile matter, 74·45% total carbon, calorific value 9750 B.Th.U. per lb. wet. The producers are water-jacketed, and have a diameter of 8 ft. 6 in.

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[9] Alting, *Het Gas*, 1917.

RECOVERY OF AMMONIA.

The proposal made by Hollingsworth, to admix up to 1% of lime with producer coal, is being strongly recommended by Government Departments with a view to an increased production of ammonia. The results obtained depend largely on the coal, but usually range between 10 to 15 lb. of sulphate per ton, or an increase of about 16%. It is usual to find that from 10% to 12% of the ammonia leaving the producers under recovery conditions is present as ammonium chloride. This comes down in the preliminary washers free from sulphate, and may either be concentrated for sale as crude or distilled with lime with other gas works ammonia liquor. It would appear that one advantage in the use of lime is in the liberation of this ammonia from the fixed salt.

Douglas and Jones claim to increase the ammonia yield from coal in coking practice[10] by using large coal. The gases have a freer travel through the coal out of contact with the coke oven walls. This cooling effect is conducive to higher ammonia yields. Zimmermann[11] gives details for increasing ammonia yields by 15% by washing out the evolved gases by means of blast furnace gases and the use of a cooling agent. Ammonia is decomposed, partly to hydrocyanic acid, at temperatures above 850° C.

OIL WASHING.

The extraction of benzol, toluol, and solvent naphtha from coal gas made on gas works and coke ovens, has been very much extended, and various competent workers have published papers containing information and data which should prove invaluable to others who have not had an opportunity of going fully into these points.

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[10] *Gas World*, Nov. 3, 1917.

[11] *Stahl und Eisen*, 1916. **36**, 573; *J*, 1916, 1098.

Edwards[12] discusses fairly fully the question of suitable scrubbers, without however indicating where his preference lies. He gives some interesting figures for extraction of benzene in washers of different numbers of chambers as compared with the tower counter-current system. Towns gas of 500 B.Th.U. net produced in horizontal and inclined retorts contained usually 0·8% by volume of benzene vapour or a partial pressure of 6·1 mm. of mercury. At the minimum summer temperature of 25° C. 6·1 mm. pressure of benzene vapour was in equilibrium with 3·75% of benzene in the creosote wash oil; 0·8% by volume was equal to 1·83 gallon per 10,000 cubic feet, and this should require a theoretical circulation of wash oil of 48·8 gallons per 10,000, or if the gas yield were 11,500 cubic feet per ton, 50 gallons per ton of coal. The actual possible yields with this quantity used in washers with one, two, four, and eight chambers together with the benzene in the oil are tabulated.

Washing system. Number of chambers.	Yield, galls. per 10,000 cub. ft.	Constitutional efficiency, %.	Concentration in oil % by vol.	Not recovered.	
				Galls.	%
1	0·91	50	1·86	0·91	50
2	1·37	75	2·81	0·46	25
4	1·59	87	3·26	0·24	13
8	1·77	93	3·63	0·06	7
Counter-current	1·83	100	3·75	Nil.	Nil.

Edwards states that the cost of steam for distillation of wash oil was usually about half the cost of recovery. Any variation in the amount of oil used not only made itself felt on the fuel account, but increases would cause the temperatures of wash oil to rise at the outlet coolers, and the efficiency of washing would be affected.

Rhead[13] has published two papers which together form an invaluable source of information on gas washing and benzol production. He discusses :—

(1) Gas washing from the standpoint of the kinetic theory, giving new data and a reliable technical method of determining vapour pressures of wash oil and crude benzol products.

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[12] *Gas World*, April 28, 1917; *Gas J.*, 1917, **138**, 187; *J.*, 1917, 539.
[13] *Gas J.*, 1917, **137**, 207; *J.*, 1917, 331 and 764.

(2) The effect of temperature on gas washing.

(3) The effect of surface contact on gas washing.

(4) The effect of quality and composition of creosote on gas washing with special reference to viscosity, on which original data is given.

(5) The effects of temperature on viscosity of creosotes and its fractions.

(6) The effect of naphthalene on the viscosity of creosote.

(7) The effect on viscosity of continual heating at 130° to 160° C.

(8) The effect of viscosity on the rate of cooling of creosote.

(9) Theoretical considerations of the effect on the gas of naphthalene in creosote, with calculated curves showing the vapour pressures of naphthalene from creosote containing various percentages of naphthalene at different temperatures.

The following curves are given :—

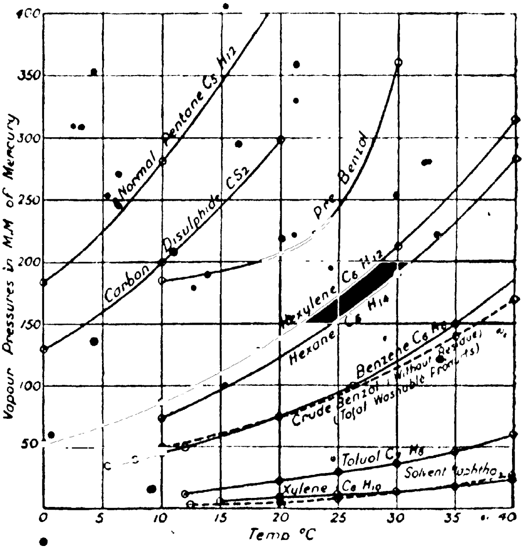

Fig. 1.—Vapour Pressures of Liquids.

The two following creosotes are discussed :—

	A.	B.
Sp. gr. ...	1·0275	0·964
H_2O	0.25 %	0·2 %
First spot	104° C	136° C.
15°–200° C	1·0 %	0·7 %
200°–220° C	7·5 %	2·0 %
220°–250° C.	47·0 %	17·6 %
250°–300° C	28·5 %	44·6 %
Residue	16·0 %	35·2 %

The oil was distilled in a 700 c.c. Wurtz flask at 2 drops per second with the thermometer in the vapour. In order to determine what the composition of a suitable wash oil having a satisfactory viscosity should be, the wash oils were fractionated (as shown) and viscosities determined. The effect on viscosity when light oils are removed by steam distillation can be seen from the following curves :—

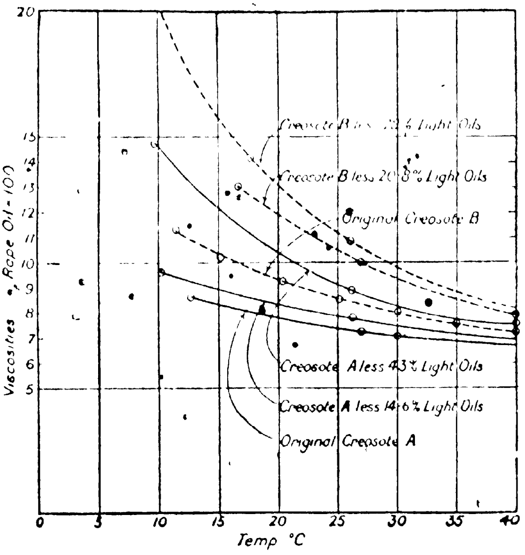

Fig. 8.—Viscosities of A and B and Residues after Steam Distillation.

The effect of viscosity on the rate of cooling of wash oil is shown by the following curve.

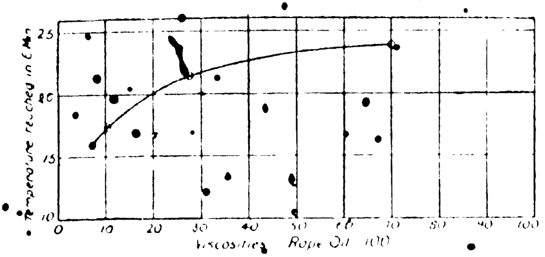

Fig. 3.—Effect of Viscosity on the Amount of Cooling in a Given Time.

Rhead submits the following conclusions

(1) The efficiency of washing is greatly improved by using a cold oil—say at 15° C—providing the creosote keeps sufficiently fluid.

(2) The lighter oils in creosote 180°–220° C help the washing process by lessening the viscosity of the creosote, but are objectionable in that they are readily distilled out by steam and contaminate the crude benzol

(3) Naphthalene helps to lessen the viscosity, and thereby helps the washing, but it very objectionable, in that it prevents good extraction of naphthalene from the gas, and may even add some to the gas under certain conditions of quantity and temperature.

(4) Creosote fractions boiling above 300° greatly increase the viscosity, and are very objectionable if present to any extent.

(5) A good creosote should remain as fluid as possible at 10°–15°, give little oil distillate when steam distilled, and have as low a naphthalene content as possible

(6) Much improved cooling of debenzolized oil from the crude still is obtained by using a creosote of which the viscosity rises very little when cooled to 10°–15°, and better temperatures are obtained for benzolized oil entering the crude still

(7) The efficiency of washing is greatly improved by increasing the intimacy of contact between the oil and gas. Washers on the spraying or atomizing principle appear to offer the best field for development in this direction—namely, an increase of surface per volume of washer and a minimum back-pressure.

(8) When using mixtures of blast-furnace and coal-tar creosotes specific gravity is no criterion as to whether a creosote is "spent" or not. Viscosity is the best test, and its magnitude should be between 8 to 9, with a maximum of 10 (rape oil=100).

(9) A sufficient quantity of creosote should be in circulation to prevent the light oils taken out and contained in the crude benzol in stock leaving a creosote of high viscosity. If light oils are sold with crude benzol, then either the creosote must be changed more frequently or the equivalent quantity of similar light oils added to take the place of those in the crude benzol.

Applebee[14] states that the most suitable wash oil should not contain any large amount of naphthalene or other solid hydrocarbon. Its specific gravity should be conveniently over 100, and its specific heat should not be too high.

The view of most other works seems to be that other factors play a more important part in gas washing than any of the above.

The aromatic series of hydrocarbons are found in but small quantities in either the tar or gas produced from vertical retorts Here are found conditions which approximate to lower temperature conditions as the volatile constituents are in contact with a comparatively small area of highly heated surfaces and the primary products of coal distillation pass away only partially "cracked"

Jones[15] has analysed the tar produced from the distillation of coal in a vacuum up to 450° C., and found it to consist of (1) unsaturated hydrocarbons, (2) naphthenes, (3) liquid paraffins (4) phenols and xylenols, (5) aromatic compounds (homologues of naphthalene), (6) pyridine, (7) traces of a solid paraffin, but benzene and its homologues were absent. From the results of the thermal decomposition of this tar at different temperatures, Jones concluded, among other things, that benzene and its homologues are chiefly formed as the result of olefinic condensation at temperatures of 700° C. and upwards To some extent they are products formed by the thermal dehydrogenation of the corresponding naphthenes. Jones[16] had previously found that the cyclo-hexanes decomposed at 490° C.-540° C. over hot porcelain and formed the gaseous product, hydrogen, methane, ethane, ethylene, and traces of acetylene and considerable quantities of benzene.

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[14] *Gas J.*, 1917, **138**, 338 ; *J.*, 1917, 635

[15] *J.*, 1917, **36**, 3

[16] *Chem. Soc. Trans.*, 1915, **107**, 1582; *J.*, 1915, 1239.

If the necessary naphthenes predominated in the primary products of coal distillation, a temperature of 500° C. upwards would give the maximum yield of benzene hydrocarbons, but apparently the olefines predominate, because the maximum benzene yield is obtained at 700° C. upwards.

The once prevalent view that acetylene was the basis of aromatic formation during coal distillation is now discredited, but it seems quite probable that an appreciable quantity of benzene is produced by the polymerisation of this hydrocarbon, which appears among the primary products of the thermal decomposition of coal.

Much light is thrown on the cracking processes that take place during high temperature carbonization if a study is made of the results obtained from the cracking of petroleum oils.

Cracking of Petroleum Oils

It has long been known that various oils, especially those in crude petroleums, when subjected to the right conditions of temperature and pressure, break down or polymerise and yield a certain proportion of benzene and its homolgues, the amount of which varies with the composition of the oil.

Rhead points out that the mode of formation of benzene, etc., during the cracking of petroleum oils is parallel to that of its formation from the cracking of the primary decomposition products of coal. These latter contain many compounds found in petroleums, such as naphthenes, paraffin hydrocarbons, olefines, etc., and since it is far easier to separate petroleums into single groups of compounds than is the case with coal, a systematic study of the thermal decomposition products of petroleum oil fractions should throw much valuable light on the mechanism of coal carbonisation.

In Russia it has long been the practice to crack petroleum oils to obtain benzene and other aromatic compounds for the dye and explosives industries, the shortage of coalfields having made such an industry of vital economic importance. Moreover, Russian petroleums, being rich in naphthenes, lend themselves admirably to benzine formation. There is little doubt that this industry, founded by the Russian chemists, led by Nikiforoff, has received a great impetus from the needs of the war.

The first systematic work in the modern era on producing aromatic hydrocarbons from petroleum, was carried out by Rittman,[17] but the large-scale installation put down at Pittsburgh as a result of his experiments has been unable to compete with other sources of benzene and toluene owing to the small yield and poor quality of the products (see p 78)

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[17] *J. Ind. Eng. Chem.*, 1915, 7, 945, *J*, 1914, 626; 1915, 1199.

The manufacture of carburetted water gas is essentially an oil-cracking process, and the evidence so far available goes to show that a good quality benzene and toluene can be obtained by washing the gas from this process In the early days of the war this source was unjustly ignored, owing to the lack of a good test for the benzol content of a gas The shortage of gas oil supplies has considerably handicapped this source in England, but it affords vast possibilities in America, the home of carburetted water gas plants

Some tests made at the Birmingham Gas Works showed that, of the oil cracked in this process 3·27% appeared as benzene and about 2% as toluene and the products were not seriously contaminated with paraffin hydrocarbons

Egloff,[18] experimenting with a low carburetted water gas plant, obtained per thousand cubic feet of gas 0·07 gallon of benzene, 0·06 gallon of toluene, and 0·01 gallon of xylene On this basis he estimates that the carburetted water gas manufactured in America if washed, would yield annually 8,689,000 gallons of benzene 7,118,000 gallons of toluene, and 1,241,300 gallons of xylene

Lessing[19] describes a form of apparatus in which vapours are absorbed by oil with which a mass of granular material has been soaked. The absorbed vapours are then distilled off *in situ* with superheated steam and condensed in a water cooled coil The apparatus is then ready for further absorption

NAPHTHALENE

This constituent of coal gas has given an increasing amount of trouble during recent years to those interested in the efficient distribution of gas The Institution of Gas Engineers have had the matter under thorough investigation and have issued a brochure on the subject.

The troubles have mainly arisen due to inefficient cooling of the gas before it leaves the works, to the elimination from the gas of those hydrocarbons which act as solvents or "carriers" of naphthalene (benzol, toluol, solvent naphtha), to increased heats and bad repair of horizontal and inclined retorts, and to the enforced use of creosotes

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[18] *Gas J.*, 1917, 138, 483.

[19] *J.*, 1917, 103

(for oil washing) which contain high percentages of naphthalene. The brochure states that the possibility of naphthalene deposition from the gas (in consumers' services and meters) depends on the amount of naphthalene in the gas, and also on the amount of vapours of the lower boiling fractions of tar which are present in the clean gas, but particularly the constituents that have boiling point approximating to that of naphthalene. Naphthalene troubles may be eliminated if the gas is sufficiently cooled and if suitable vapours are added to the gas in the most efficient way and in sufficient quantity. Methods of spraying and evaporating suitable solvents are fully discussed, and also the point at which the addition of solvents is best effected.

PURIFICATION OF COAL GAS

Espenhahn[20] suggests improvements in Feld's zinc and iron thiosulphate methods of purifying gas. The gas is washed with ammonium thiosulphate-polythionate solution (ammonium thiosulphate treated with sulphur dioxide). This is brought into intimate contact with the gas in vertical rotary washers. The reaction results in the absorption of ammonia and part of the hydrogen sulphide. By withdrawing portions of the solution as it becomes concentrated and treating with sulphur dioxide and heat, the polythionates are converted into sulphates. A fertilising salt is recovered by evaporation, and the process claims to solve the problem of utilising the sulphur content of the coal for the fixation of ammonia without first forming sulphuric acid.

Wanner[21] proposes to use wood charcoal in small pieces for the removal of carbon bisulphide and hydrogen sulphide from crude coal gas. The charcoal after use may be revivified by heating to 105° C. for two days.

W. S. Curphey[22] discusses the direct recovery process for ammonia and its effect on oxide purification. He states "an attempt has been made to co-ordinate the data relating to periods of good and bad working, and the analysis of the data yields results of positive value." It would appear that in every case failures of the purifiers occurred when the make of gas was on the increase at the end of the period, and that the use of fresh and highly moist oxide is attended with risk when it coincides with periods of maximum make of gas and an exceptional

[20] *J.*, 1917, 488–489.

[21] *J. Gasbeleucht.*, 1915, 156; *J.*, 1917, 75.

[22] *See J.*, 1915, 1001; 1917, 907.

amount of ammonia is needed at such times to maintain the oxide in a neutral condition. It is confidently believed that when the oxide has become dried and is better matured results will show improvement. Fresh oxide should be stocked and brought into condition during the summer months. Small diameter pipes may with advantage be connected from inlet ammonia scrubber to boxes, so that a little ammonia may be allowed to pass and neutralise any soluble salts of iron present in the oxide.

MINERAL OIL.

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The need of a more general and better understanding of the meaning or application of the names applied here and in America to the different grades of mineral oil products has become insistent during the past few years, owing to the difficulties which have arisen from the existing confusion of terms and from the introduction of new products, cognate in use, though not in origin, with the old. The efforts so far made to secure agreement in nomenclature have been small and limited in scope, but they are suggestive and hopeful in that they may lead to greater efforts, which the Society of Chemical Industry might well initiate, to form by collaboration with the Institution of Petroleum Technologists and kindred bodies in America and other English-speaking countries an International Committee on the Nomenclature of Mineral Oils. The same or an allied committee is also imperatively required to deal with standardisation in the arbitrary methods of testing such oils. The matters in question are essentially for chemists to discuss and determine, though in view of the large use which engineers make of mineral oils, and the good work in the standardisation of engineering materials which has already been accomplished by the Engineering Standards Committee, it is desirable that this Committee should have representation on any International Committee on the Nomenclature and Testing of Mineral Oils which may be formed by technical chemists.

NOMENCLATURE

A few instances of the existing confusion of terms may appropriately be cited. At one end of the range of products of mineral oil we have those of which the chief demand is now for use as motor spirit. Primary products of petroleum available for use as motor-spirit pass under a great variety of names, *e.g.*, petroleum spirit, petroleum naphtha, gasolene, petrol, carburine, benzoline, benzine, &c., and it would be difficult to draw a hard and fast line between any two of these terms. "Gasolene" is peculiarly American, and is associated with the former extensive use of air-gas in places remote from town gas supplies. 'Petrol,' originally applied by one firm of producers to its product, has been extended by motor car users in this country to petroleum spirit in general. 'Petroleum spirit' has the advantages of clarity and official recognition, but the general public everywhere prefers a single word, and it should not be difficult for an international committee of chemists, backed by the big oil producers and distributors, to restrict the choice to 'gasoline' and 'petrol,' and ultimately to make the use of one only of these terms universal for motor spirit derived directly from petroleum. Especially is it desirable, once for all, to get rid of the term 'benzine,' which leads to confusion between the petroleum spirit to which it is applied and the chemical entity benzene, which is obtained commercially from coal gas and coal tar. Unfortunately, "benzine" is almost universally adopted in the oil fields and crude oil refineries as a general term for the lighter distillate from the crude oil, and it is likely to prove very difficult to displace it for use in this connection. An unobjectionable alternative for works' use is 'spirit,' which is already applied to some extent and is well understood in the oil districts, and every effort should be made to extend its use in preference to 'benzine.'

"Motor spirit" becomes, however, a more comprehensive expression, including besides petroleum spirit or petrol, benzole, shale naphtha, brown coal naphtha, naphtha from low temperature coal distillation processes, spirit or naphtha obtained by the cracking of heavy oils, crude alcohol, and mixtures of two or more of these products with or without admixture of a certain proportion of kerosene or the like. Distinctive and brief terms for most of these products are necessary, and there should be some co-ordination among them. Benzol stands by itself, and alcohol also stands apart. The grades sold as motor fuel may conveniently be termed "motor benzol" and "motor alcohol." The spirit or naphtha from shale, brown coal, cannel and coal distillation might well be known as 'shale motor spirit,' 'coal motor spirit,' &c.

Passing to the other end of the scale of products of mineral oil, viz., the heavy bitumens and asphalts, an attempt was made by the Engineering Standards Committee in 1916 to furnish a British Standard Nomenclature for these materials, so far as their use for road purposes is concerned. The attempt was praiseworthy, but the recommendations made have not proved generally acceptable, for reasons which chemists will readily divine. Especially were the recommendations at variance with definitions which are widely accepted in America.

No definition appeals to the technical chemist which does not embody a statement of physical or chemical properties by which the materials comprised under it can be distinguished with certainty from all other materials. It is often difficult with materials which occur in nature as the product of the action of subterranean heat and pressure on other substances to suggest physical or chemical tests by which such materials may be indubitably distinguished from artificial products derived from the same or other original substances, but in cases where the difficulty is insuperable it follows that the natural and the artificial materials will be indistinguishable also in use. Pending a wider knowledge of the essential properties and composition of many natural products, it is still the practice of the engineer, or less reluctantly than of the chemist, to specify that some material required in certain constructional work must be obtained from a certain locality, ofttimes from a particular works or quarry. As a confession of ignorance or laziness on the part of the person responsible for the specification the practice is illuminating, but its true defects become revealed when the work carried out with the material happens to fail, and the chemist is called in to ascertain not simply whether it had or had not certain essential or desirable characteristics, but whether its properties tally with those of other samples or of genuine material from the specified locality of origin.

The asphalt industry is replete with instances of the practice in question, and more research is needed on the part of the physicist and chemist before the restrictive practice can become unnecessary. Vested interests in a local product of well-deserved repute naturally are opposed to any definition which presumes that a like article might be obtainable from another source. The last few years, however, have so greatly extended the sources of supply of asphaltic materials and the means of refining, blending and treating them, that the monopoly of superiority of the more vaunted products is seriously threatened, and there is no question that origin will in the future be regarded as of less import than defined physical and chemical characteristics. The new outlook will naturally entail a correlative revision of nomenclature and definitions.

The following suggested terminology and definitions of mineral oil products, in regard to which there has been much confusion hitherto, may help to pave the way to a common understanding (many terms which are generally well understood and in regard to which confusion rarely arises are omitted).

Motor Spirit.—Volatile liquid, which, without preheating, is fit for use as fuel in internal combustion engines other than of the Diesel type.

Petrol.—Motor spirit obtained as a primary product of the distillation of petroleum. Synonymous with gasoline and petroleum spirit. Other expressions, which should be discarded for the same product or certain grades of it are: naphtha or petroleum naphtha or mineral naphtha, benzoline, benzine, carburine. Grades of petrol should be primarily distinguished by reference to the percentage of distillate which they afford below certain temperatures, *e.g.*, 120, 145, 170 C., and secondarily only by vapour pressures, ignition temperatures, specific gravity, &c.

Shale Motor Spirit.—Motor spirit derived from the volatile products of the distillation of oil shales. Synonymous with shale naphtha.

Coal Motor Spirit.—Motor spirit derived from the volatile products of the distillation of coal and cannels otherwise than in gas retorts and coke ovens.

Cracked Motor Spirit.—Motor spirit obtained by the cracking of the less volatile mineral oils, tar oils, &c.

Motor Benzol.—Motor spirit derived from coal gas or its condensation products.

Motor Alcohol.—Motor spirit obtained by fermentation or distillation from carbohydrates, &c., and consisting chiefly of alcohols.

Kerosene.—A purified fraction of mineral oil fit for use for lighting purposes in lamps with wick feed.

Fuel Oil.—Liquid fuel not sufficiently volatile for use as motor spirit, but fit for direct combustion in furnaces, Diesel engines, &c. Includes heavy grades of crude petroleum, distillates and residua, shale, cannel, and coal oils and distillates, tars, tar oils, &c.

Motor Oil.—Oil primarily intended for the lubrication of the cylinders of internal combustion engines.

Cylinder Oil.—Oil primarily intended for the lubrication of the cylinders of steam engines.

Bitumen.—A comprehensive term for mixtures of hydrocarbon products containing more or less oxygen and/or sulphur, which are soluble in carbon disulphide. (Should be restricted to highly viscous liquids and solids; the term has no useful application from the technical and scientific standpoint to gases and highly mobile liquids, such as benzene, though legal luminaries have sought to include such bodies under the term.)

Natural Bitumen.—Bitumen obtained by simple extraction or evaporation from materials found in nature, without constitutional change by oxidation or other chemical action.

Pyro-Bitumen. Bitumen which is insoluble in carbon tetrachloride. (Synonymous with carbenes.)

Petrolenes (or *Malthenes*). Constituents of bitumen which are soluble in hexane.

Asphaltenes. Constituents of bitumen which are insoluble in hexane, but soluble in carbon tetrachloride.

Coal Bitumen. Bituminoid material which is soluble in pyridine, but insoluble in carbon disulphide.

Asphalt. Bitumen in intimate admixture with finely divided mineral matter, the mixture containing no chemically uncombined carbon (*i.e.*, "free carbon").

Rock Asphalt. Limestone or other inorganic mineral matter found in nature impregnated with bitumen.

Tar. The matter (freed from water) condensed from the volatile products of the destructive distillation of hydrocarbon matter, whether this be contained in coal, wood, peat, oil, or other material.

Pitch. The solid or semi-solid residue from the partial evaporation of bituminous material. Especially from the partial evaporation of tars.

STANDARDIZATION OF TESTING.

The standardization of empirical methods of testing the physical and chemical characteristics of mineral oil, &c., has been discussed in several quarters in the course of the year, and urgently calls for reference to an authoritative committee such as the Society could form from its members with a few collaborators drawn from other bodies.

E. L. Lomax has discussed the question so far as motor spirit, especially petrol, is concerned.[1] He proposes to substitute for the Redwood and Engler methods of carrying out the distillation test one in which the essential difference is the introduction of a 4-pear Young dephlegmator column. The proposed method has obvious advantages, but lacks the simplicity of apparatus of the others, and, in common with them, has the disadvantage of using too small a quantity (*i.e.*, 100 c.c.) of petrol to admit of rapid determination of the specific gravity and other properties of the several distillates. The information which is thereby obtained affords a valuable guide to the differentiation of motor spirits from various sources. In practice 500 c.c. appears to be the most suitable quantity of motor spirit to take for a distillation test.

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[1] *J. Inst. Petrol. Tech.*, 1917, **4**, 6; *J.*, 1918, 116 A.

N. A. Anfilogoff has described a modification of the Redwood method, in which he retains the ordinary Engler distillation flask, but sets the thermometer so that the bulb (which is 4 ins. from the zero of the scale) is ½ in. below the opening of the side tube of the flask.[2] He distils at the rate of two drops a second. The writer has used substantially the same procedure for many years past, the essential difference from Anfilogoff's method being the employment of a larger flask with 500 c.c. of motor spirit and the rate of distillation being restricted to one drop a second.

Recent Investigations and their Import

J. H. Coste has determined the minimum flashing point and the solidification point of certain motor spirits and of acetone.[3] Three petrols flashed well below 0° C., while the solidification point of one of them was −128·6° C. Coste concludes that petrol is dangerous to handle near a flame at any temperature likely to occur in Great Britain, but unlike benzol it will not give trouble through freezing even at Arctic temperatures.

Lomax[4] has also reviewed methods of determining the sulphur content of motor spirit. He commends a modification by Esling of the combustion method, in which the motor spirit after admixture with alcohol is burnt from a small wick lamp in a good current of air. Such a method is undoubtedly more trustworthy for motor spirits of tolerably low sulphur content than determination of the sulphur through the products of combustion of the spirit in the bomb calorimeter. It does not, however, strike the technical chemist as affording an ideal solution of the analytical problem involved, and there is hope that ultimately a direct oxidation method may be made available for the rapid and accurate estimation of the total sulphur in motor spirit and similar highly volatile combustible liquids.

A matter which calls for further investigation is the relative bearing of different physical properties of the several constituents of motor spirit on ease of starting an internal combustion engine when cold. It is well known that of two different brands of petrol, both giving practically the same distillation curve, one affords easy starting while the other presents great trouble in this respect, though once the engine is running there is nothing to choose between the two brands. Sometimes, indeed, the petrol which is troublesome at starting is distinctly superior, if the engine becomes overheated, in respect of liability to pre-ignition. It is not certain on what characteristics of petrol ease of starting depends, for though the vapour pressure at low temperature and vapour density are undoubtedly of primary importance, it seems likely that the temperature of ignition plays a part here, as it certainly does in determining the liability to pre-ignition. The spontaneous ignition temperatures of liquid fuels have been investigated by H. Moore, especially, however, in regard to fuel oil suitable for use in Diesel engines.[1] His work, however, leads to the general conclusions, which are applicable to motor spirit also, that aromatic compounds have much higher ignition temperatures than aliphatic compounds, saturated compounds higher than unsaturated, and compounds containing simple molecules higher than similar compounds containing more complex molecules. These conclusions should be very helpful to compounders of petrol substitutes, whose empirical processes [illegible] should not be despised, since there is little question that in the near future the bulk of the motor spirit supplied will be prepared by blending products of different origin, composition and character. Apart from the benefit to be derived from the utilisation by this means of large quantities of materials unsuitable alone for use as motor spirit, it seems probable that a full knowledge of the properties and behaviour of different series of hydrocarbons, &c., will lead to the preparation of motor spirit by blending which will be superior to any straight-run petrol when all essentials of a good motor spirit have been taken into account.

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[2] *J.*, 1918, 21A.

[3] *Analyst*, 1917, 42, 168; *J.*, 1917, 587.

[4] *J. Inst. Petrol. Tech.*, 1917, 4, 19; *J.*, 1918, 116A.

A valuable contribution to methods of analysis of mineral oil has been made by S. E. Bowrey in the course of developing a ready and exact process for the estimation of toluene in crude petroleum.[2] The total proportion of aromatic hydrocarbons in a mixture may be ascertained by sulphonation or nitration, but the relative proportions of the different aromatic hydrocarbons cannot be determined through either of these methods. Bowrey extracts a fair sample of the aromatic hydrocarbons, which is available for further study by fractionation, by liquid sulphur dioxide applied at about −35° C. He has devised an arrangement of apparatus which is convenient for the extraction and the recovery of the aromatic hydrocarbons from the extract. The method should prove useful in investigating the composition of "petrol substitutes," in which benzols or cracked spirits have been blended with kerosene, &c., as well as in the study of those crude petroleums and distillates which contain notable proportions of aromatic hydrocarbons. The schemes for the estimation, by inference from fractionation curves, of the proportions of benzene, toluene, and xylenes in crude benzols, &c., are not generally applicable to the estimation of aromatic hydrocarbons in petroleum spirit.

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[1] *J.*, 1917, 109.

[2] *J. Inst. Petrol. Tech.*, 1917, **3**, 2[illegible]

Methods of testing are of relatively great importance in connection with mineral oils, because many of them have been devised with the immediate purpose of elucidating the qualities of the oils on which their successful technical application depends. Thus the testing of the viscosity of oils, the consistency of bitumens and the hardness of asphalts has received further attention during the past year. Several new forms of viscosimeter have been described, of which that designed by F. M. Lidstone is specially noteworthy.[7] It may be applied to a very small quantity of oil, and to give specific viscosities in terms of water at a defined temperature, while by calibration against a Redwood, Engler, or other similar instrument, its readings may be translated into Redwood, &c., "degrees." It has the advantage of being low in first cost. Other forms of viscosimeter have been devised by C. H. Briggs,[8] W. M. Grosvenor,[9] R. Dubrisay[10] and C. Browning.[11] While it is now generally recognised that viscosity in itself has little relation to "oiliness" or lubricating value, it is a physical quality which has an important bearing on the choice of oils for use as vehicles, fluxes, &c. The effect of dissolving solids in an oil on its viscosity has been studied to some extent in connection with solution of naphthalene, &c., in tar oils, but it is a subject which would well repay further study, especially in regard to the preparation of tars and bitumens for road treatment. The viscosity, or rather the consistency, of such materials intended either for the surface-dressing of roads or the production of bituminated macadam, is now commonly checked in this country by the use of Hutchinson's viscosity gauge, a nickel silver sinker of defined dimensions and form, which is compared before issue with a reference standard. An instrument of wider range, known as the Crosby Consistometer, has been introduced in the United States by W. W. Crosby.[12] It involves the use of a series of plungers of which those of smaller cross-section are intended for semi-solid and solid bitumens and asphalts, and the larger ones for heavy oils, &c. It appears to give results which are more in keeping with the variations in behaviour of pitches and asphalts in actual use than are readings obtained with the Dow and New York Laboratory penetrometers, which have hitherto been regarded as standard instruments for this class of work. The needle, with its irregularly coned point, which is the operative factor of these penetrometers, cannot be regarded as satisfactory either in principle or in practical application, and it is not surprising that technical men in this country wish to secure general recognition for a penetrometer of more scientific design and more utilitarian value than the American standard instruments. A penetration machine designed by J. Hutchinson having a plunger one centimetre in diameter with flat end weighted with ½, 1 or 2 kilos, has been found by the writer to show clearly differences in the consistency of pitches, &c., which are not indicated by the New York needle penetrometer, and to give less erratic readings. In all comparative testings of the physical properties of pitches and bitumens it is of paramount importance that the temperature of the material under test should be exactly controlled and the volume and shape of the test portions clearly defined and adhered to.

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[7] *J.*, 1917, 270 and 1918, 148r.

[8] *J.*, 1917, 1031.

[9] *J.*, 1917, 1065.

[10] *J.*, 1917, 1123.

[11] *J.*, 1918, 22 A.

[12] *Proc. Amer. Soc. Testing Materials*, 11, 191.

Attempts to assess the "oiliness" or lubricating value of machine oils, &c., continue to be made, and with increasing measure of success. H. K. Moore and G. A. Richter have described a device designed to compare the internal friction or power consumption and the durability of lubricating oils,[13] and J. A. Lowry has produced a bearing with means of comparing the resistance to rotation of the shaft when different oils are used under different load.[14] The resistance to pressure of films of oil has an important bearing on its lubricating qualities, and ready means of measuring this are being proposed by investigators both here and in the United States. The emulsifying quality of oils has also been the subject of investigation in the United States. P. H. Conradson has described a simple method of investigating the emulsifying and demulsifying value of oils,[15] and W. H. Herschel has prepared for the Bureau of Standards a Technical Paper (No. 86) dealing with the resistance of oils to emulsification.[16] Both these authors deal only with the emulsifying of lubricating oils, and not with the preparation of emulsions other than for lubrication. There has, however, been considerable advance in this country, since the outbreak of war, in the preparation of emulsifying and water-soluble oils for disinfecting and other uses, though comparatively little has been published in regard thereto.

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[13] *Met. and Chem. Eng.*, 1917, **16**, 692; *J.*, 1917, 975.

[14] *J.*, 1917, 1085.

[15] *Amer. Soc. for Testing Materials*, June, 1916; *J.*, 1917, 232.

[16] *J.*, 1917, 497.

An extremely valuable paper has quite recently been read by A. E. Dunstan and F. B. Thole before the Institution of Petroleum Technologists on the "Relation between Viscosity and the Chemical Constitution of Lubricating Oils." After reviewing previous researches, and their own work extending over many years, these authors arrive at the conclusions that A lubricating oil should contain a certain proportion of unsaturated hydrocarbons, viz., as high a proportion as is compatible with little susceptibility to oxidation, polymerization, gumming and reactivity. The physical condition of a good lubricant is probably colloidal.

Cracked Motor Spirit.

The Rittman process for the cracking of heavy petroleum with a view to the production of motor spirit, consisting mainly of aliphatic hydrocarbons or, alternatively, of benzols, which those experienced in the manufacture of gas from oil marvelled to hear had received special protection from the Government of the United States, has apparently gone into oblivion, at least so far as aliphatic motor spirit is concerned. Its failure emphasizes the futility of proceeding to exploit a technical process without seeking advice and collaboration from those who have had life-long knowledge and experience in the industries it touches. Other cracking processes, following sounder principles, have had more successful, if less dramatic, careers during the past year. Many of them have been reviewed by Lomax, Dunstan and Thole in a paper[17] on the "Pyrogenesis of Hydrocarbons," which embodies an exhaustive historical summary by E. L. Lomax of cracking processes brought forward up to nearly the close of the year 1916, and a considered account by A. E. Dunstan and F. B. Thole of the general principles and considerations underlying the procedure of cracking. The paper concludes with a comprehensive bibliography of the subject.

Persons unfamiliar with earlier features of the production of kerosene and of oil gas are apt to think that the cracking of oil is a purely modern development, whereas the recent efforts to develop cracking processes are directed merely to effecting such modifications as are necessary to furnish a predominance of aliphatic motor spirit in the resultant product. For many years past the superintendent of carburetted water gas installations has known that he can produce at will gas and tar saturated with aromatic hydrocarbons, which can be recovered and fractionated to commercial grades of benzol, &c At the outset of the war gas chemists pointed to the cracking of petroleum oil in existing or specially modified gas plants as the most promising means of securing a large production of toluol and it is now only a question of price whether toluol so produced can hold its own in the market against the by-product toluol of the coal gas and coke-oven industries Egloff has recently drawn attention to the possibilities of utilizing the carburetted water-gas plants in operation in the United States for the production of toluol by the cracking of solvent naphtha in the presence of water gas[18] The cracking of oil for the production of aliphatic motor spirit however is a somewhat more difficult proposition than that of the manufacture by the cracking of heavy grades of petroleum of either kerosene or benzols It is comparatively easy to produce by cracking a good yield of "spirit" having the required range of distillation vapour pressure &c, but commonly such spirit contains a large proportion of relatively unstable hydrocarbon compounds, with the result that on keeping it undergoes changes which cause gumminess and darkening of colour. Methods of refining in use for petroleum distillates if applied to such cracked crude spirit are very wasteful and expensive owing to the ease with which a large proportion of the compounds of the spirit are attacked, and generally leave a product which is still unstable and malodorous Nevertheless skilful control of the cracking process overcomes most of the difficulty which the pioneers and the present-day novices find in producing a stable and refinable spirit by the cracking of heavy petroleum

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[17] *J. Inst. Petrol. Tech.*, 1916, **2**, 374; *J.*, 1917, 20.

Many studies have been made of the effect of variations in temperature and pressure on the nature and yield of cracked spirit but generally speaking little has been published in regard to the effect of variations in the rate of flow of the material through the cracking apparatus which is usually dependent on the arbitrarily chosen diameter of vessels, tubes, &c, and the freedom or otherwise of the latter from packing, whether or no ostensibly having a catalytic action. Among the studies worthy of attention are those by Egloff, Twomey, and Moore on the effect of variation of time and temperature (over the range 400°–750° C.) on the cracking in an 8-in clear tube of a Pennsylvanian gas oil[19]; by G Egloff on the decomposition of a mixture of pentanes and hexanes at pressures from 1 to 12 atmospheres and temperatures from 450° C. to 725° C.[20]; by Downing and Pohlman on the production of tar and gas from gas oil cracked in atmospheres of different gases[21]; by Zanetti and Egloff on the decomposition of benzene in an iron tube furnace heated to from 500° to 800° C.[22]; by R. Cross on the cracking of petroleum in the liquid phase at a pressure of 30 atmospheres and a temperature not exceeding 400° C.[23], by Egloff and Moore on the effect of aluminium chloride and other catalysts on the conversion of Pennsylvanian kerosene into cracked spirit[24]; by Egloff and Twomey on the formation of benzene, toluene, and xylene by cracking a Pennsylvanian gas oil in an 8-in. clear tube at temperatures ranging from 1400° to 1500° F.[25], and by L. B. Cherry on the conversion of kerosene to motor spirit by subjecting its vapour in the presence of methane to the discharge of a high-tension, high-frequency oscillating current.[26] In addition to the foregoing technical papers, patent literature during the past year has been particularly rich in specifications claiming improvements in and new methods of producing motor spirit from heavy grade mineral oils. The specifications are too many even for enumeration here, and there is no evidence as yet that novel principles of proved value have been covered by any of them which are not also dealt with in the technical communications already quoted.

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[18] *J, Ind Eng Chem*, 1918, **10**, 8, *J*, 1918, 116A

[19] *Met and Chem Eng*, 1916, 523, *J*, 1916, 1209

Asphalt.

War conditions have militated against any great advance in connection with paving, and the plentiful supplies of asphaltic materials from Mexico, the United States, and elsewhere which were promised to this country a few years ago have been curtailed, while certain other supplies have been held up altogether. Comparatively little research work has been carried out recently on asphalts, but two papers have been published by Clifford Richardson, in which he brings forward interesting theories of the nature and behaviour of asphalt.[27] In one he points out that carbon dioxide forms a high proportion of the

[20] *Met. and Chem. Eng.*, 1916, 692; *J.*, 1917, 76.

[21] *Gas J.*, 1917, **137**, 24; *J.*, 1917, 125.

[22] *J. Ind. Eng. Chem.*, 1917, **9**, 350; *J.*, 1917, 499.

[23] *Met. and Chem. Eng.*, 1917, **16**, 643; *J.*, 1917, 860.

[24] *Met. and Chem. Eng.*, 1916, **15**, 67; *J.*, 1916, 882.

[25] *Met. and Chem. Eng.*, 1916, **15**, 15; *J.*, 1916, 882.

[26] *Amer. Electro Chem. Soc.*, Oct., 1917; *J.*, 1917, 1266.

[27] *Met. and Chem. Eng.*, 1917, **16**, 25, and 1917, **17**, 650; *J.*, 1917, 204, and 1918, 59A.

gases associated with asphaltic oils and bitumen, whereas it does not occur with purely paraffin oils. In the second paper he regards an asphalt pavement as a colloidal solution in which the suspended matter, owing to the great viscosity of the continuous phase, may be of considerable coarseness, and makes certain deductions from this premise. Brooks and Humphrey[28] have dealt with the effect of sulphur on the oxidation or hardening of residual oils, showing that the presence of sulphur during blowing greatly accelerates the production of hard bitumen. Reeve and Lewis have compared the effects of prolonged exposure to the air on different bitumens, and have found a correlation between the results and the behaviour of the different bitumens when used in a road surface.[29] The changes observed are accounted for in part only by evaporation; probably polymerisation and intermolecular reactions come into play also. C. F. Mabery has made comparison of different bitumens, especially gilsonite and elaterite.[30] He concludes that gilsonite is more closely related than elaterite to petroleum, though the hydrocarbons obtained from them on distillation indicate a common origin.

OIL FUEL.

Developments in connection with the use of mineral oil as fuel for boilers and Diesel engines have been restricted during the period under review by the appropriation of the greater part of the available fuel oil for naval use. An interesting paper has been given by J. S. S. Brame on "Liquid fuel and its combustion," which naturally deals chiefly with petroleum and the different burners and devices used for its combustion as furnace fuel.[31] A point of considerable importance in regard to supplies of fuel oil is their content of sulphur. The Admiralty Specification now prescribes a maximum of 3%, whereas the United States Bureau of Mines has fixed a maximum of 1%. The greater latitude allowed by the British Admiralty may probably be traced to a desire to draw supplies from Mexico and English shales rather than to any technical ground for a belief that less than 3% of sulphur is harmless, whereas somewhat more is injurious to boiler plates and tubes. F. M. Perkin has reviewed the whole question of sulphur in mineral oils in an exhaustive paper,[32] in which he deals more particularly with the elimination of sulphur from oil obtained from shale which is rich in sulphur. Many patents have been taken out for processes for eliminating the sulphur from the oil yielded by Dorsetshire shale, which is exceptionally rich in sulphur compounds. Some aim at treating the shale before retorting; others provide for treatment in the retorts; yet others treat the vapours before they are condensed, while several treat the crude oil itself. The problem, so far as Dorsetshire shale is concerned, cannot yet be regarded as satisfactorily solved.

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[28] *J. Ind. Eng. Chem.*, 1917, 9, 746; *J.*, 1917, 997.

[29] *J. Ind. Eng. Chem.*, 1917, 9, 743; *J.*, 1917, 998.

[30] *J. Amer. Chem. Soc.*, 1917, 39, 2015; *J.*, 1917, 1123.

[31] *J. Inst. Petrol. Tech.*, 1917, 3, 194; *J.*, 1917, 703.

[32] *J. Inst. Petrol. Tech.*, 1917, 3, 227; *J.*, 1917, 702.

OIL PRODUCTION.

It is impossible to give complete statistics of the mineral oil production of the world, and the imports and exports of different countries since the outbreak of war. Tolerably full figures have been collected by D. Ghambashidze and given in a paper read before the Institution of Petroleum Technologists on March 19, 1918. His figures for the year 1916 are given below, with the addition of Japan.[13]

Country	Barrels (of 42 galls.) produced in 1916.	Relative production in other years (1916 = 100).		
		1914.	1915.	1917 (estimated).
United States	300,767,158	88·36	93·46	113·64
Russia	72,801,116	92·06	94·16	96·15
Mexico	39,817,402	53·91	82·52	150·69
Dutch East Indies	13,174,399	97·36	94·02	110·05
Rumania	10,298,208	123·37	116·82	106·82
Galicia	6,461,756	77·89	64·36	106·82
Japan	2,911,426	90·95	100·79	

The exports and imports of mineral oil in different countries have been affected still more than the total production by war conditions. The exports from the United States in 1916 were 11·8% more than in 1915,[14] but on the other hand exports from Russia to other countries were almost entirely cut off, though the export from the Caucasus to other parts of Russia showed a large increase. Everywhere the value of the oil produced and exported has shown an enormous increase as compared with pre-war years, the increase varying in different countries from 20 to 100%. This increase in the value of oil, coupled with transport difficulties, has stimulated efforts at local production even in countries like Great Britain, which is relatively ill-favoured in respect of mineral oil resources. The prospects of oil production in this country have been discussed with increasing animation in a number of technical papers, of which one by W. H. Dalton,[35] and one by Craig, Perkin, Berry, and Dunstan[36] are the most authoritative. Recently a Committee has been appointed by the Institution of Petroleum Technologists to obtain evidence in respect of the quantity of cannel coal and allied minerals available in Great Britain as a source of motor spirit, fuel oil, and other products, and to formulate a scheme for the utilisation of such supplies. This has been followed by the appointment by the Minister of Munitions in agreement with the Colonial Office and the Petroleum Executive, of a Committee under the chairmanship of Lord Crewe, to consider a report (which has not been made public) rendered by the Petroleum Research Department on the production of fuel oil from home sources. It is noteworthy that there is no mineral oil expert or chemist on this officially appointed Committee.

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[13] *Japanese Bureau of Mines, Mineral and Metal Output in 1916*; J., 1917, 1133.

[14] J., 1917, 284.

Broadly it may be said that so far as published reports of investigations (as distinct from surmises) show there is little hope of obtaining crude petroleum in any appreciable quantity by drilling in Great Britain. Distillation of shales, cannels, and coal is capable of giving a greatly increased output of oil, particularly of fuel oil, and it is merely a question of whether labour and capital are better expended in this than in other directions at the present time, and to what extent the present emergency warrants the introduction of plant and methods which will be unable to face free competition if ever called upon to do so. It may be said without fear of authoritative contradiction that there is undoubtedly permanent scope for the exploitation of a certain amount of cannel, &c., for oil production in this country, and provided the cannel is selected with discretion and appropriate plant is used for its distillation an industry may be created which can face free competition. But the plant must be chosen and worked with due regard to the particular cannel which is to be handled and the by-products it is capable of yielding; no one type of plant or mode of working will ensure the best results from all the available cannels, waste coals, &c. Also to attempt to create an oil industry by the distillation of all and sundry waste coals, slack, cannels, &c., is to court a colossal failure, which will impede legitimate progress in oil production in this country for many years to come.

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[35] *J. Inst. Petrol. Tech.*, 1917, **4**, 137; *J.*, 1918, 116A.

[36] *J.*, 1918, 175A.

COLOURING MATTERS AND DYES.

By Gilbert T. Morgan, D.Sc., F.R.S.,

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In the Report for 1916 the writer put forward the conjecture that the new epoch in the history of coal-tar dyes, ushered in by the war, would find the local demands for dyewares in process of becoming supplied by local producers. This anticipation is being rapidly realised, especially in those countries in which industrial enterprises are less affected by war conditions. American manufacturers have had the great advantage of an ante-war period of more than two years during which they were free from the distractions arising from the mobilisation of their man-power and the diversion of their manufacturing activities into war industries. Full advantage was taken of this breathing space in dealing with the shortage of dyes. Before the war America used per annum approximately £3,000,000 worth of dyes, of which an amount costing only about £600,000 was made in the United States. The remainder was imported, the bulk of this supply coming from Germany. At present there are 22 American firms producing direct coal-tar products or "crudes," 40 factories manufacturing intermediates, and 16 turning out finished dyes. The capital at the disposal of these undertakings exceeds £10,000,000, and already 75% of the home requirements in intermediates and dyes are being supplied. With the aid of large research staffs the rapid production of the remainder is confidently anticipated. The export of dyewares from the United States for the fiscal year ending June 30, 1917, was valued at £2,340,000, being more than double that of the preceding year.

The vitality of a national industry in dyes is based on the economic production of coal-tar crudes and intermediates. Increasing numbers of intermediates are being manufactured in America, including aniline and benzidine and their homologues, *p*-nitroaniline, the naphthols and naphthylamines and their sulphonic acids, H-acid and other aminonaphtholsulphonic acids. The vegetable colours of America are also being exploited, and mineral lakes and pigments are being handled by specialists in this branch of the dye trade. An increasing export trade in these colours and intermediates with the United Kingdom is in progress.

Many dye plants have been established in Japan, the largest being the Japan Dyestuff Manufacturing Co. When these factories are in full working order this country will be independent of foreign supplies.

In spite of the ravages of war, the chemists of France are making a close and logical study of the dye problem, and at the St. Denis works and in other factories great advances are being achieved.

The Italian development is less advanced, the problem being intimately bound up with the question of fiscal tariffs on the crudes and intermediates to be imported.

The Russian effort has been stultified by the revolution, and the capture of Riga by Germany has involved the loss of at least one aniline factory.

With the foregoing tendencies in course of development the problem facing English dye producers is the sufficiently onerous task of making the British Empire self-contained in the matter of synthetic dyes and other coal-tar products. As regards war requirements this result has been achieved, for British manufacturers are producing sufficient colouring matters to dye not only all the uniforms of the army and navy, but also many of the naval and military uniforms of the Allies. So far as the exigencies of war permit, steps are being taken to cope with the more complex demands which dye users will make on the resumption of peace. In this direction progress is being made with increasing rapidity, but much remains to be accomplished.

A remarkably successful effort at the rapid production of complex dyes has been achieved by the Solway Dyes Co. (Morton Sundour Fabrics, Ltd.), who had produced indanthrene yellow in small quantities four months after the outbreak of war, and who were making this vat dye in bulk in February, 1915. They have since added other anthraquinone dyes to their list, including alizarin sapphirol, which was achieved in March, 1916.

The production of special dyes for the colour-sensitising of photographic plates was before the war a small but very important monopoly of the German colour makers. The secrets of this art were rediscovered in 1916 in the chemical laboratory of Cambridge University, and platemakers were supplied from this source with these invaluable products. Parallel researches on these dyes were also carried out during the same period in the University of Leeds[1] and Leeds Technical School.

Messrs. Levinstein, Ltd., who are making full use of their recently acquired indigo factory at Ellesmere Port, are now self-contained as regards dyewares, intermediates, and the mineral acids required in the production of these synthetic products. This firm, in association with Messrs. Claus, have produced large quantities of dyes for military and naval requirements, thus assisting very materially not only in equipping the British fighting services, but also the Allied armies.

British Dyes, Ltd., who have added alizarin delphinol to their growing list of anthraquinone dyes, are now trebling the pre-war output of colours formerly produced by their predecessors, Messrs. Read Holliday and Sons, Ltd. Other dye-producing firms are displaying commendable enterprise, and among those who are rapidly increasing their range of dyes are Messrs. L. B. Holliday and Co. (Huddersfield) and Messrs. Brotherton and Co., Ltd. (Port Rainbow). Several manufacturers of explosives are following the example of the two foregoing firms in the hope that the production of intermediates, dyes, drugs, and other fine chemicals may furnish a post-bellum occupation for their plant, capital, and staffs.

At the present time, however, the chief industrialised nations of the world are in a state of war, and although scientific investigation is in progress in all those countries which have not actually been devastated by hostile invasions, yet on both sides current research is diverted to an ever-increasing extent into warlike channels in response to the inexorable pressure of national emergency.

COAL-TAR CRUDES.

The demand for those direct tar products or coal-tar crudes which furnish the basis of military high explosives is still insistent. Synthetic phenol has been produced on an extensive scale to eke out the supply of coal-tar carbolic acid and synthetic processes have been devised for increasing the available supply of benzene and toluene. Xylene has been utilised for T.N.X. (trinitroxylene), and the nitro-derivatives of the plentiful hydrocarbon, naphthalene, have also been employed as explosives.

The Supply of Benzene and Toluene.

Benzene and toluene are still urgently needed for military requirements, and the search for additional supplies of these hydrocarbons still continues in various directions. Demethylation of the higher benzenoid hydrocarbons contained in solvent naphtha has been studied with the object of producing the greatly needed lowest homologues. The cracking of this aromatic oil gives results which compare very favourably with those obtained from paraffin and naphthene oils. The optimum temperatures for the production of benzene and toluene are respectively 800° and 750° C., the oil being passed through a heated steel tube (11½ ft. × ·8 in. diameter) under a pressure of 11 atmospheres. About 25% of the solvent naphtha is demethylated, the percentage yields of benzene and toluene at the foregoing temperatures being 15·9 and 20·6 respectively. The recovered oils are increased in specific gravity, this change indicating the formation of polycyclic aromatic hydrocarbons of high molecular weight.[2]

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[1] Harrison and Bottomley, *Report*, *Leeds*, Nov. 1916. W. J. Pope, *Brit. J. Phot.*, Jan. 1917; *J.*, 1917, 163.

This cracking process for solvent naphtha is a reaction giving similar results to that of the reversed Friedel-Crafts reaction, which has also been recommended as a means of obtaining toluene and cumene from cymene, now obtainable in large quantities as a by-product of the sulphite cellulose process. The reversal is brought about by the action of aluminium chloride on cymene dissolved in excess of benzene. The reaction is complicated and involves demethylation of cymene and methylation of benzene: $C_6H_4 \cdot C_3H_7 \cdot CH_3 + C_6H_6 = C_6H_5 \cdot CH_3 + C_3H_7 \cdot C_6H_5$. Ninety grams of cymene in 900 grams of benzene gave, on boiling for 10 hours with 4·5 grams of aluminium chloride, a yield of toluene and cumene corresponding with 80% of the amount calculated from the foregoing equation.[3]

The production of toluene by the direct Friedel-Crafts reaction on benzene and methyl chloride was referred to in last year's report.[4]

The Friedel-Crafts reaction applied to aromatic alcohols in the presence of benzene leads to the production of diphenylmethane together with smaller amounts of *o*- and *p*-dibenzylbenzene, anthracene, and a hydrocarbon $C_{27}H_{24}$, probably tribenzylbenzene, or methylene-bis-diphenylmethane. Excess of benzene favours the main reaction.[5]

Coal-tar naphtha, distilled under a pressure of 35 lb. per sq. in., is converted into a lighter spirituous fraction, from which toluene can be obtained, and a heavier oil which is redistilled under atmospheric pressure, the naphtha recovered in this rectification being again submitted to the pressure distillation process.[6]

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[2] Egloff and Moore, *J. Ind. Eng. Chem.*, 1917, **9**, 40; *J.*, 1917, 128.

[3] Bœdtker and Halse, *Bull. Soc. Chim.*, 1916, **19**, 444; *J.*, 1917, 129.

[4] Sifton, U.S. Pat. 1216574; *J.*, 1917, 382.

[5] Huston and Friedemann, *J. Amer. Chem. Soc.*, 1916, **38**, 2527; *J.*, 1917, 25.

[6] Gartley, U.S. Pat. 1225237; *J.*, 1917, 638; *cf.* Anderson, Eng. Pat. 108508; *J.*, 1917, 1001.

Benzene and toluene are obtained by passing vapours of hydrocarbons of high boiling point, such as solvent naphtha, through a heating plant at 600°–700° C.[7] Coal-tar naphtha heated to a high temperature yields a certain proportion of toluene.[8]

Crude petroleum from Ripi, an Italian product, has been cracked so as to yield 10% of tar rich in light oil, containing benzene and toluene.[9]

The oil-washing of coal gas was commenced by the Gas Light and Coke Co., London, in 1913, and the practice is recommended as a permanent feature of gas manufacture in the interests of national economy. A "green oil" of sp. gr. 1·098 and yielding 80% of distillate up to 370° C., is recommended as the washing oil by the use of which "strong" benzols can be produced requiring less sulphuric acid and alkali than are usual in the washing process.[10]

The efficiency of creosote in the washing process as a washing medium for extracting benzene from coal gas, has been examined in detail from chemical and physico-chemical points of view.[11]

A partial hydrogenation of the benzene molecule is effected by passing dry ammonia through benzene containing calcium shavings. Ammonia is absorbed forming a calcium-ammonia compound, $Ca(NH_3)_4$, and this compound acts as reducing agent towards benzene producing dihydrobenzene.[12]

$$Ca(NH_3)_4 = Ca(NH_2)_2 + 2NH_3 + H_2.$$
$$H_2 + C_6H_6 = C_6H_8.$$

This process may find further application in the production of hydro-aromatic hydrocarbons and their derivatives.

COAL-TAR INTERMEDIATES.

The three principal methods of converting coal-tar crudes into intermediates, namely nitration, sulphonation, and chlorination, have all found employment in the manufacture of military explosives, and during the period under consideration these processes have been extensively studied with this object in view. Nitration is an essential step in the production of all coal-tar explosives. Sulphonation is required in the usual process for preparing synthetic phenol and the formation of phenolsulphonic acids is an intermediate stage in the production of picric acid.

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[7] Alexander, U.S. Pat. 1230975; *J.*, 1917, 922.

[8] O. B. Evans, U.S. Pat. 1230087; *J.*, 1917, 866.

[9] Rodano, *Annali Chim. Appl.*, 1917, **8**, 7; *J.*, 1917, 1091.

[10] W. G. Adam, *Gas J.*, 1917, **137**, 343; *J.*, 1917, 331.

[11] Rhead, *Gas J.*, 1917, **137**, 207; *J.*, 1917, 338.

[12] Dumanski and Zvereva, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 994; *J.*, 1917, 286.

The chlorination of benzene gives chlorobenzene which serves as a starting point for picric acid, tetryl, and hexanitrodiphenylamine.

Nitro compounds.

The nitration of aromatic compounds is still a subject of great industrial importance, and many improvements have been devised in the technique of this process. Continuous nitration plants are now in operation whereby the output of nitro compounds, such as trinitrotoluene, is greatly increased and the amounts of nitric and sulphuric acids required are reduced to a minimum. Speed in nitration is attained by the employment of special cooling pipes and coils.[13]

The immense demand for trinitrotoluene has rendered it desirable to nitrate toluene rendered impure by paraffins. The nitration is effected in two stages, the mononitrotoluene being separated from paraffin by solution in an equal volume of concentrated sulphuric acid.[14] Impure tar is nitrated by weak nitric acid at 10–60° C. The strength of acid is increased and the temperature allowed to rise to 70–90° C. The mixture is left and the lower aqueous layer drawn off, the upper semi-solid layer being treated with strong nitric and fuming sulphuric[15] acids at 95–105°.

The problem of obtaining the more highly nitrated derivatives of the hydrocarbons is largely a matter of efficient dehydration, especially in the later stages of nitration. Nitrosyl sulphate is used instead of concentrated sulphuric acid to absorb the water formed during nitration. *m*-Dinitrobenzene (one part) is slowly heated with nitrosyl sulphate (two parts) till dissolved, when nitric acid (two parts) is added and the mixture maintained at 100–120° until *s*-trinitrobenzene is produced.[16]

The additive compounds of *s*-trinitrobenzene and the aromatic hydrocarbons and amines have been extensively studied.[17] These crystalline additive compounds may prove useful in characterising aromatic hydrocarbons. The anthracene compound, for instance, is bright red.

The orientation of the entrant nitro-group is greatly influenced by the nature of the radicals already present in the aromatic nucleus.

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[13] J. W. Leitch and F. R. Lankshear, Eng. Pat. 105775; *J.*, 1917, 633.

[14] Flurscheim, U.S. Pat. 1225321; *J.*, 1917, 679.

[15] McJick, U.S. Pat. 1225347; *J.*, 1917, 638.

[16] Heinemann, Eng. Pat. 101216/1915; *J.*, 1917, 78.

[17] Sudborough, *Chem. Soc. Trans.*, 1916, **109**, 1339, 1349; *J.*, 1917, 128.

The well-known nitration of phenol leads to a mixture of *o*- and *p*-nitrophenols. Nitration of phenyl phosphate, $PO(OC_6H_5)_3$, gives exclusively tri-*p*-nitrophenyl phosphate, from which pure *p*-nitrophenol is obtained on hydrolysis. Cresol when nitrated yields 3-nitro-*p*-cresol ($CH_3 : OH : NO_2 = 1 : 4 : 3$), whereas *p*-cresyl carbonate, $OC(OC_6H_4.CH_3)_2$, gives rise to a dinitro ester containing each nitro-group in the ortho position to the methyl group, so that by hydrolysis 2-nitro-*p*-cresol is obtained. The free hydroxyl group has a far greater directing influence than methyl as regards substitution, but when the hydroxylic hydrogen is replaced as in *p*-cresyl carbonate the influence of the methyl group becomes predominant.[18]

The great demand for picric acid has led to its production from various gums and gum-resins, either alone or dissolved in concentrated acetic acid, by treatment with nitric acid below 40° C. Any unconverted gum or gum resin is removed and the solution of picric acid or other nitrophenol is boiled and allowed to crystallise.[19]

The nitration of chlorobenzene is of the utmost industrial importance because it affords a means of obtaining 2.4-dinitrophenol, picric acid, the mononitrophenols and nitro- and dinitro-anilines besides other important intermediates required in the manufacture of dyes and explosives. It is nitrated with facility by heating with sodium nitrate and sulphuric acid (sp. gr. 1·84).[20]

Carbazole is being increasingly employed as a colour producing intermediate. It is nitrated to 3-nitrocarbazole by treatment with nitric acid of 10% concentration.[21] This process is applicable to the halogen derivatives of carbazole.

The nitration of toluene has been studied in detail by many chemists during the past three years, and the experimental conditions for obtaining the best yields of *o*- and *p*-nitrotoluene, 2.4-dinitrotoluene and 2.4.6-trinitrotoluene have been determined. Yields of 55 and 60% of the *o*- and *p*-mononitro-compounds have been obtained by Kidokoro, who has also examined the nitration of *m-tert.*-butyltoluene to its trinitro-compound (artificial musk).[22]

The action of concentrated sulphuric acid on aromatic nitro-derivatives at high temperatures is of interest in view of the use of this dehydrating agent in nitration. At 195° C. sulphuric acid and nitrobenzene interact very vigorously. The products are a black amorphous solid (10%) and *p*-aminophenol-*o*-sulphonic acid (8%), together with 50% of unchanged nitrobenzene. The black substance dissolves completely in aqueous sodium hydroxide, but only partially in concentrated sulphuric acid; it is slightly soluble in nitrobenzene, pyridine, trimethylamine, or ammonia. Similar black substances are produced from nitrobenzene and sulphuric acid in the presence of anthraquinone, β-aminoanthraquinone, or anthracene. These black products can be reduced to form vat dyes having an affinity for cotton.

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[18] Holleman and Hoeflake, *Rec. Trav. Chim. Pays Bas*, 1917, **36**, 271; *J.*, 1917, 207.

[19] H. C. Miller and H. G. Irlam, Eng. Pat. 104352, 1916; *J.*, 1917, 499.

[20] Ellis and Wells, U.S. Pat. 1220078; *J.*, 1917, 499.

[21] Act.-Ges. f. Anilinfabr., Ger. Pat. 295817; *J.*, 1917, 542.

[22] *J. Chem. Ind., Tokyo*, 1917, **20**, 460; *J.*, 1917, 1065.

Nitrobenzene alone steel gray vat dye.
Nitrobenzene + anthraquinone steel gray vat dye.
Nitrobenzene + β-aminoanthraquinone brown vat dye.
Nitrobenzene + anthracene brown vat dye.

This reaction appears to be general for homocyclic nitro compounds.[23]

Sulphonation and Sulphonic Acids.

The sulphonation of benzene, which is of importance as being the first step in the production of synthetic phenol, has recently been the subject of several researches.

In the case of the more volatile aromatic hydrocarbons boiling below 200° C., sulphonation is effected by passing the vapour of the substance into the heated sulphuric acid. The process is applicable to benzene when the vapour is introduced into strong sulphuric acid heated gradually from 100° to 185° C. so long as absorption takes place.[24] Benzene vapour is passed for 27 hours through 100 parts of sulphuric acid (sp. gr. 1·753) at 120° C. and excess of the hydrocarbon removed by a current of hot air. On cooling, 130 parts of crystalline benzenesulphonic acid separate. The process is rendered continuous by means of a suitable plant, the distillate of benzene and steam is condensed and separated, the hydrocarbon being dried and again utilised in the sulphonation.[25]

Considerable ingenuity has been shown in endeavouring to overcome the practical difficulty of separating arylsulphonic acids from sulphuric acid. The former is extracted with a solvent, such as benzene, which is not very miscible with sulphuric acid. The benzene solution is then treated with a base forming a salt insoluble in the solvent. This process has been applied to the separation from sulphuric acid of the mono- and di-sulphonic acids of benzene.[26] Naphthalene-β-sulphonic acid is separated from sulphuric acid by solution in toluene and obtained in solid form on cooling this solution.[27]

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[23] M. L. Crossley and C. B. Ogilvie, *J. Amer. Chem. Soc.*, 1917, **39**, 117; *J.*, 1917, 209.

[24] D. Tyrer, Eng. Pat. 103204 of 1916; U.S. Pat. 1210725; *J.*, 1917, 208.

[25] Comp. des Produits Chimiques d'Alais et de la Camargue, Eng. Pat. 101973; *J.*, 1917, 705.

The sulphonation mixture after liming is agitated without previous filtration with sodium sulphate. All the calcium present is converted into calcium sulphate, and on filtration the filtrate contains the sodium salt of the arylsulphonic acid.[28]

Sodium hydrogen sulphate ("nitre cake") has been utilised in sulphonation. After dehydration to disulphate (pyrosulphate) it is dissolved in concentrated sulphuric acid, and the dehydrated and unsulphonated synthetic dye is added to the solution. After thorough mixing, the mass is dissolved in water, limed out, and the filtrate evaporated to yield the salts of the sulphonated dye.[29]

The methods of heating and stirring sulphonation pans have been under consideration recently. Up to 100° C. warm water or steam is used for heating. Above 110° high pressure steam or superheated water can be used. The pan is made of cast iron, with wrought iron steam pipes imbedded in its wall. The use of superheated steam ceases to be economical as the temperature rises. Hot mineral oil is utilisable, and is circulated through the jacket and through a heated coil. U-shaped stirrers and propeller agitation produce efficient mixing, especially if placed eccentrically in the sulphonation pan.[30]

Halogen Derivatives of the Aromatic Hydrocarbons.

Chlorobenzene has become an important intermediate, and its manufacture forms the subject of several recent investigations.

Plant has been devised for chlorinating benzene in the presence of an iron catalyst, the process being conducted so that strong chlorine comes into contact only with fresh benzene. Cooling appliances are used to maintain the temperature at 15° C., and the formation of higher chlorinated products is minimised by allowing the hydrogen chloride formed in the reaction to dilute the chlorine.[31]

The reactions taking place in the chlorination of benzene by chlorine obtained from the electrolysis of hydrochloric acid are very complicated, especially when the electrolyte is heterogeneous. Homogeneous solutions of benzene and hydrochloric acid in a common solvent such as glacial acetic acid gave, with a platinum anode, more satisfactory results. Progressive chlorination leads successively to chlorobenzene, *p*-dichlorobenzene, 1:2:4:5-tetrachlorobenzene, hexachlorobenzene, and pentachlorophenol; chloranil is always present as a by-product. Owing to the presence of acetic acid pentachlorophenol is partly converted into pentachlorophenyl acetate. The conditions favourable for a high yield of chlorinated products are high current density, low concentration of benzene, and high temperature. In these conditions almost pure hexachlorobenzene is procurable.

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[26] L. M. Dennis, U.S. Pats. 1211923, 1212612, 1227252, 1229593; *J.*, 1917, 208, 382, 705, 866.

[27] Dennis, U.S. Pat. 1228414; *J.*, 1917, 866.

[28] Sachs and Byron, U.S. Pat. 1207798; *J.*, 1917, 129.

[29] Kendall, U.S. Pat. 1217462; *J.*, 1917, 500.

[30] F. Pepe, *Met. and Chem. Eng.*, 1917, **17**, 177; *J.*, 1917, 1042.

[31] Coutagne, Fr. Pat. 480151; *J.*, 1917, 125.

The electrolytic chlorination of toluene is more complicated, for unlike the case of benzene light has a prejudicial effect and electrolysis should be effected in the dark. The stages of chlorination are as follows: *o*- and *p*-chlorotoluene, 2:4-dichlorotoluene, 2:4:5-trichlorotoluene, pentachlorotoluene, 2:4:5-trichlorobenzylidene chloride, pentachlorobenzylidene chloride, 2:4:5-trichloro-3:6-dihydroxybenzylidene chloride, and hexachlorobenzene. The degree of chlorination is determined mainly by current density, but side-chain substitution does not occur till three chlorine atoms have entered the nucleus. Nascent chlorine liberated electrolytically seems responsible for nuclear chlorination, whilst accumulations of molecular chlorine lead to attack on the side chain.[32]

The foregoing results indicate the difficulty of restricting chlorination to the production of the lower chloro-derivatives, and for this reason indirect chlorination is sometimes employed.

Toluene-*p*-sulphonic acid or its chloride or amide is dissolved in sulphuric acid and the solution treated with chlorine, and the resulting 2-chlorotoluene-4-sulphonic acid is heated in steam when the sulphonic group is removed hydrolytically and *o*-chlorotoluene is produced.[33]

Sulphonic radicals in the sympathetic ortho- and para-positions with respect to amino-groups, but not when in the apathetic meta-positions, can be displaced quantitatively by the halogens. Bromine reacts with these sulphonic acids in aqueous solutions, chlorine is effective in glacial acetic acid, and iodine is active when presented in the form of iodine monochloride. With 2:6-dibromosulphanilic acid or 4:6-dibromoaniline-2-sulphonic acid bromine yields 2:4:6-tribromoaniline and sulphuric acid. Chlorine gives a mixture of chlorodibromoanilines and tribromoanilines. The *o*-sulphonic group is more readily displaced than when in the para-position. Carboxyl groups in *o*- or *p*-positions with respect to amino-radicals are replaceable by bromine, but with greater difficulty; the displacement by chlorine or iodine either fails entirely or takes place to an insignificant extent.[34]

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[32] Fichter and Glantzstein, *Ber.*, 1916, **49**, 2473; *J.*, 1917, 207.

[33] B.A.S.F., Ger. Pat. 2946[illegible]; *J.*, 1917, 286.

At present bromination is a matter of somewhat academic interest owing to the shortage of bromine throughout the world outside the German Empire. An ingenious process of brominating aromatic hydrocarbons has been devised recently, which has the merit of introducing the whole of the bromine into the nucleus without loss of hydrogen bromide. This substitution is effected by the combined action of bromine and nitric acid, commencing in the cold and completing the reaction by raising the temperature. The hydrobromic acid generated as the by-product in bromination is continually oxidised to bromine by the nitric acid. It is, therefore, obvious that the process can be carried out by hydrogen bromide and nitric acid, a convenient strength being 40 hydrobromic acid and nitric acid (sp. gr. 1·35). By this treatment benzene yields bromobenzene and dibromobenzenes, whereas toluene furnishes *o*-bromotoluene and 3.4-dibromotoluene and finally pentabromotoluene. The reaction has been extended to the xylenes, mesitylene, and ethylbenzene.[35]

Iodination of the aromatic hydrocarbons is practicable with a mixture of iodine and nitric acid. Benzene gives iodobenzene, toluene furnishes a mixture of *o*- and *p*-iodotoluene, the xylenes, ethylbenzene, mesitylene, and thiophen yield iodo-derivatives, but with the higher hydrocarbons nitration occurs as well as iodination; naphthalene gives iodo- and nitro-naphthalene; anthracene is oxidised to anthraquinone. Nitrogen iodide or iodine and potassium iodide solution with strong ammonia are effective iodinating agents on the phenols. Phenol gives triiodophenol, whereas *o*- and *p*-nitrophenols furnish diiodo-derivatives.[36]

Benzyl chloride is produced by treating a mixture of toluene and bleaching powder or other suitable chlorine compound with sulphur dioxide to liberate chlorine, the product being separated by distillation.[37]

Synthetic Phenol

Synthetic phenol required in the manufacture of picric acid is generally produced by the fusion of sodium benzenesulphonate with alkali. Much attention has been devoted to this fusion with the object of increasing the yield, diminishing the cost of raw materials, and making the process as continuous as possible.

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[34] Sudborough and Lakhumalani, *Chem. Soc. Trans.*, 1917, **111**, 41; *J.*, 1917, 333.

[35] Datta and Chatterjee, *J. Amer. Chem. Soc.*, 1916, **38**, 2545; *J.*, 1917, 26.

[36] Datta, Chatterjee and Prosad, *J. Amer. Chem. Soc.*, 1917, **39**, 435, 441.

[37] Conant, U.S. Pat. 1233986; *J.*, 1917, 1002.

Calcium benzenesulphonate treated in aqueous solution with sodium sulphate yields calcium sulphate and sodium benzenesulphonate, the latter being fused with caustic soda. The fused mass is dissolved in water and acidified with carbon dioxide and sulphur dioxide derived from a mixture of calcium carbonate and calcium sulphite by the action of sodium hydrogen sulphate. This double decomposition leads to calcium sulphate and sodium sulphate. On passing the foregoing gases into the alkaline solution of the melt, phenol is liberated and sodium sulphite and sodium carbonate are produced. These salts, on treatment with lime, yield caustic soda and a mixture of calcium carbonate and calcium sulphite. This mixture can be used for producing a further evolution of carbon dioxide and sulphur dioxide. The other by-products can also be utilised in subsequent operations, so that the whole process becomes regenerative and economical.[38]

A cyclic process for phenol and other aromatic hydroxy derivatives is brought about by the interaction in aqueous solution of sodium phenoxide and benzenesulphonic acid (freed from sulphuric acid, *cf.* page 92). This interaction gives the phenol and sodium benzenesulphonate, the latter when fused with caustic alkali yielding sodium phenoxide to which the first reaction can be applied.[39]

The alternative route to synthetic phenol from chlorobenzene which was referred to in last year's report[40] has again received attention. A mixture of chlorobenzene (1 mol.), caustic soda (2 to 3 mols.), and water (about 20 mols.) is heated under pressure at 300° C. in a suitable apparatus arranged for continuous operation. A solution of sodium chloride and phenoxide results from which phenol is liberated by acid.[41]

The lower phenols are produced from the less volatile tar acids by spraying them with a jet of hydrogen into a chamber containing a nickel catalyst maintained at 600–650° C.[42]

Phenol is obtainable from the cresols by fusing these with excess of caustic soda or potash and adding an oxidising agent such as copper oxide, or a peroxide of lead, manganese, barium, iron, etc. The fused mass is powdered and heated at 300° C. in carbon dioxide, when phenol distils over, or the intermediate hydroxybenzoic acids are freed from the melt by acid and heated at 250° with crude anthracene oil, when carbon dioxide is liberated and phenol distils over.[43]

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[38] D. Tyrer, U.S. Pat. 1210725; Eng. Pat. 104220; *J.*, 1917, 208.

[39] Dennis, U.S. Pat. 1227894; *J.*, 1917, 866.

[40] *Ann. Rep.*, 1916, 75.

[41] Aylsworth, U.S. Pat. 1213142, 1213143; *J.*, 1917, 382.

[42] Ramage, U.S. Pat. 1208833; *J.*, 1917, 208.

Salicylic Acid and other Hydroxycarboxylic Acids.

The production of dry sodium phenoxide (phenolate) required in the manufacture of salicylic acid is effected by mixing intimately in a specially constructed grinding ball-mill equivalent quantities of phenol and caustic soda with about 5% of sodium sulphite, the mixture being meanwhile heated at 250–280° C. The steam escapes through a hollow trunnion of the mill, and the dry product is cooled *in vacuo* to prevent absorption of moisture.[44] This dry sodium phenoxide is placed in a rotating autoclave, carbon dioxide is introduced, avoiding rise of temperature. When absorption has almost ceased the pressure of carbon dioxide is increased to more than 100 lb. per sq. in., the gas supply is then interrupted, and the autoclave heated to 120–140° C.[45] The crude sodium salicylate thus produced is dissolved in nine parts of water, the solution, made faintly acid with sulphuric acid, is pumped through a column of granulated zinc, and then, after heating to 80–100° C., through a tower containing a mixture of 95% of charcoal and 5% of zinc. The filtrate when acidified furnishes colourless salicylic acid.

When a fused mixture of o-cresol and caustic soda is electrolysed the corresponding hydroxybenzoic acid is produced. Sodium salicylate is obtainable by electrolysing with 5–8 amps. per sq. dcm. in the anode compartment a mixture formed by adding *o*-cresol (one part) slowly to caustic soda (three to five parts) and water (one part), and then heating at 240°–250° C. Nickel, nickel-steel, or iron electrodes are employed.[46]

1.5-Dihydroxynaphthalenedicarboxylic acid, a naphthalene analogue of salicylic acid, is produced from 1.5-dihydroxynaphthalene by the action of solid sodium bicarbonate in the presence of an indifferent medium such as trichlorobenzene or nitrobenzene.[47]

The polyhydric phenols are fairly reactive towards the alkali bicarbonates. With potassium bicarbonate at 120° C. under atmospheric pressure, resorcinol yields 2.4- and 2.6-dihydroxybenzoic acid, whereas pyrogallol furnishes 2.3.6-trihydroxybenzoic acid. At 200° C. under pressure catechol is converted into its dicarboxylic acid and resorcinol yields α-resodicarboxylic acid. At 260°–270° quinol gives rise to a dicarboxylic acid. At 230°, 1:5-dihydroxynaphthalene gives its dicarboxylic acid. This acid and its alkali salts dye wool in yellow shades, which turn into brown dyeings on treatment with chromic acid. 1:6-Dihydroxynaphthalene furnishes a yellow monocarboxylic acid.[48]

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[43] Ferrisse, Eng. Pat. 108938; *J.*, 1917, 1001.
[44] Everitt, Eng. Pats. 105611, 105614; *J.*, 1917, 584, 614.
[45] Everitt, Eng. Pats. 105612, 105613; *J.*, 1917, 584.
[46] Pomilio, Eng. Pat. 1037[illegible]9; *J.*, 1917, 3[illegible]2.
[47] F. von Hemmelmayr, Ger. Pats. 296[illegible]35, 296501; *J.*, 1917, 590.

Reduction

A drastic method of reduction which leads to the conversion of anthraquinone into anthraquinol and anthrone, and of benzophenone into β-benzpinacolin, is brought about by dissolving the ketonic substance in excess of concentrated sulphuric acid, and then adding aluminium powder, with cooling and stirring. Copper is sometimes employed as the reducing metal.[49]

When acetic or benzoic acid is present the acetyl or benzoyl derivatives of the hydroxy-compound is produced. In these circumstances anthraquinone yields diacetyl- or dibenzoyl-anthraquinol.

Certain aromatic nitro-compounds, such as *p*-nitrotoluene, *p*-nitrophenol, or *p*-nitroanisole, are reduced to amines by hydrogen and platinum black. The aromatic nitroso-compounds behave similarly. The terpenoid nitroso-derivatives are in these circumstances reduced to hydroxylamines; for instance, 8-nitrosomenthone yields 8-hydroxylaminomenthone.[50]

Electrolytic Reduction of Nitro-Compounds

The specific action of the electric current on aromatic nitro-compounds in the cathodic cell has long been known to yield aminohydroxy-derivatives, although these products are accompanied by amines. The formation of the latter substances is diminished, and the production of aminohydroxy-derivatives increased, by using a cathode containing two metals. For this purpose an alloy may be used or a simple metallic cathode may be present, the second metal being introduced in the form of its salt dissolved in the electrolyte. Alternatively the cathode may be of carbon, both metals being deposited thereon during electrolysis. Nitrobenzene, reduced through a plain lead cathode, gives *p*-aminophenol and aniline in the proportion of 2 to 3, whereas a copper-lead cathode yields these products in the proportion of 5 or 6 to 1. Other cathodes are copper with lead and arsenic in the electrolyte, lead with bismuth, or copper with mercury or with tin or arsenic.[51]

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[48] *Monatsh. Chem.*, 1917, **38**, 77; *J.*, 1917, 1268.

[49] Eckert and Pollak, *Monatsh. Chem.*, 1917, **38**, 11; *J.*, 1917, 866; Ger. Pats. 190656, 261542.

[50] Cusmano, *Atti R. Accad. Lincei*, 1917, [v], **26**, ii, 87; *J.*, 1917, 1267.

Production of Aromatic Amines.

In the last Report reference was made to the direct reduction of the vapours of aromatic nitro-derivatives with hydrogen in the presence of catalysts. This process is still under examination, and it has now been found that the hydrogen may be mixed with carbon monoxide and a zinc compound may be employed to activate the copper catalyst.[52]

Attempts have been made to bring about direct combination between benzene and ammonia, but even at 700° C. only a trace of aniline is formed. In presence of freshly reduced iron, copper, or nickel somewhat larger amounts of aniline were produced.

A general method of producing N-alkylarylamines arises from the interaction of a primary arylamine and an aliphatic aldehyde in the presence of a reducing agent in a medium not possessing a strongly acidic character. The anhydroaldehyde-amine or Schiff base produced from the amine and aldehyde is simultaneously reduced to alkylaromatic amine. Methylaniline is conveniently prepared by this process, the first-formed methyleneaniline being reduced to the secondary base by zinc dust and caustic soda at 90° C.[53]

The foregoing process leads to methylaniline free from dimethylaniline, whereas the interaction of molecular proportions of aniline and dimethyl sulphate in benzene solution does not yield exclusively methylaniline methylsulphate, $C_6H_5N\,CH_3,CH_3\cdot HSO_4$, but gives a mixture of crystalline aniline methylsulphate and mono- and di-methylanilines. The course of this action is followed by means of hypochlorite colour reactions. In neutral solution, aniline only gives a reddish purple coloration. In slightly acid solution, a deep orange yellow is characteristic of dimethylaniline, whilst aniline and methylaniline give an indigo blue which is most pronounced with the former base if the hypochlorite is added last. Methylaniline gives its most distinctive reaction in faintly alkaline solution, a white precipitate slowly developing a navy blue coloration fading to yellow.[54]

Diphenylamine is greatly in request not only as a colour-producing intermediate, but also as a stabiliser for high explosives. Its production from aniline and aniline hydrochloride is greatly facilitated by the use of suitable catalysts. Aniline when heated with ferric chloride, finely divided copper, and iodine is converted into diphenylamine.[55]

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[51] Soc. Chem. Ind. Basle, U.S. Pat. 1207798; *J.*, 1917, 129.

[52] B.A.S.F., U.S. Pat. 1207802; *J.*, 1917, 78.

[53] G. T. Morgan, Eng. Pat. 102834, *J.*, 1917, 207; U.S. Pat. 1221077; *J.*, 1917, 499.

[54] Shepard, *J. Amer. Chem. Soc.*, 1916, **38**, 2507; *J.*, 1917, 26.

A yield of 6[illegible] % of phenyl-α-naphthylamine calculated on α-naphthol is obtained by heating for 10 hours at 300° C. α-naphthol (1 mol.), aniline (2 mols.), and calcium chloride (1 mol.). The product after removing unaltered reagents is distilled *in vacuo* in a current of carbon dioxide or hydrogen.[56]

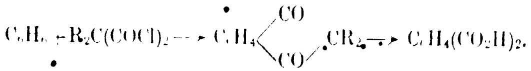
The production of aromatic amines by heating chloro-derivatives with aqueous or alcoholic ammonia under pressure, sometimes in the presence of a copper catalyst, is being increasingly utilised on an industrial scale. 2-Aminoanthraquinone is thus prepared from 2-chloroanthraquinone and aqueous ammonia either with or without copper or copper salts.[57] Derivatives of 2-aminoanthraquinone are produced by the same process.

Condensations

Ketones of the thiophen series are prepared in satisfactory yield by heating thiophen with aliphatic and aromatic acid chlorides in the presence of phosphoric oxide. Condensation takes place with elimination of hydrogen chloride on heating the reagents in a reflux apparatus.[58]

Benzoylation of 2-hydroxyanthraquinone and its derivatives takes place on heating these substances with 10 to 15 parts of benzoic acid. Sulphuric acid accelerates the condensation but its presence is not essential.[59] This process obviates the use of benzoyl chloride.

Aromatic polycarboxylic acids are readily produced by nitric acid oxidation of dialkylindanediones, which are obtained by condensing dialkylmalonyl chlorides with aromatic hydrocarbons in the presence of aluminium chloride.



$$C_6H_6 + R_2C(COCl)_2 \longrightarrow C_6H_4\begin{matrix} \diagup CO \diagdown \\ \diagdown CO \diagup \end{matrix} CR_2 \longrightarrow C_6H_4(CO_2H)_2.$$

This example leads to phthalic acid, but other less accessible polycarboxylic acids are obtainable by this process, for example 1.2.3.4-

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[55] B. J. Flurscheim, U.S. Pat. 1212928; *J.*, 1917, 382.

[56] Katayama, *J. Chem. Ind. Tokyo*, 1917, **20**, 353; *J.*, 1917, 865.

[57] Farbenfabr. vor. F. Bayer, Ger. Pat. 295624; *J.*, 1917, 542.

[58] Steinkopf, Ger. Pat. 297203; *J.*, 1917, 638.

[59] Wedekind and Co., Ger. Pat. 297261; *J.*, 1917, 638.

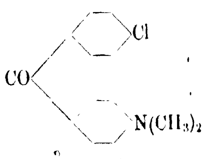
benzenetetracarboxylic acid (mellophanic acid) from *p*-xylene, and 1.2.3.5-benzenetetracarboxylic acid (prehnitic acid) from *m*-xylene.[60]

p-Hydroxybenzoyl-*o*-benzoic acid, $HO{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$, the intermediate product in the formation of phenolphthalein from phenol and phthalic anhydride, has been employed in the synthesis of mixed phthaleins.[61] Resorcinol gives rise to two isomeric phenolresorcinolphthaleins, whereas α- and β-naphthols yield the corresponding α- and β-naphtholphenolphthaleins.

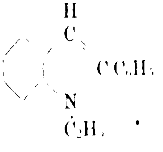
DI- AND TRI-PHENYLMETHANE DYES.

An interesting development in the synthesis of diphenylmethane colouring matters arises from the employment of indole derivatives in these condensations.

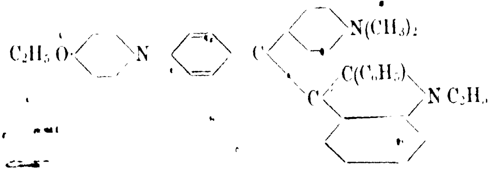
An indyl dye of this new type is produced by condensing 4-chloro-2-methyl-4-dimethylaminobenzophenone (I) with N-ethyl-α-phenylindole (II). The resulting intermediate is heated with *p*-phenetidine and the second product (III) is sulphonated. The sulphonic acid dyes wool in reddish blue shades very fast to light.[62]



I



II



III

The employment of *o*-cresotic acid in the production of triphenylmethane dyes is still a subject of investigation. Chlorinated xylenes are further substituted in the side chains when exposed to light and chlorine at 100°–130°. The products treated with sulphuric acid are converted into chlorinated dialdehydes or arylaldehydocarboxylic acids. These substances are condensed with *o*-cresotic acid and the resulting leuco-derivative oxidised with sodium nitrite in concentrated sulphuric acid. These dyes from chlorinated arylaldehydocarboxylic acids and *o*-cresotic acid dye wool in brown-red shades from acid baths, these tints being converted by chroming into bright violet-blue dyeings very fast to washing and milling.[63]

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[60] Freund and Fleischer, *Z. angew. Chem* 1916, **29**, 421; *J*, 1917, 77.

[61] Orndorff and Murray, *J. Amer. Chem. Soc* 1917, **39**, 679; *J.*, 1917, 542.

[62] Stock and Nicodemus, (M. L. & B.), U.S. Pat 1217238; *J.*, 1917, 449; Ger. Pats 290065, 295495; *J.*, 1916, 531; 1917, 287

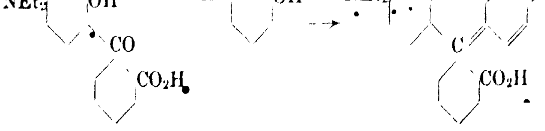
Acridine Dyes as Disinfectants and Germicides.

The success attending the use of acriflavine, diaminomethylacridinium chloride, has led to investigations on acridine dyes with the object of finding other equally efficacious products.[64] The cadmium and silver salts of 2.7-dimethyl-3.6-diaminoacridine (methylated at the acridine nitrogen) have been specially claimed as having a well-marked disinfecting action. The silver salt is a brownish-red powder soluble in water, alcohol, acetone, ethyl acetate, sulphuric acid, or acetic acid. It checks the growth, even in very dilute solutions, of such bacteria as *streptococci* or *splenitis* bacilli.[65]

Pyrone Colours.

A useful summary of the chemistry of the natural and synthetic pyrone colours has been compiled this year by Everest. The synthetic pyrones are divisible into two series: the diphenylmethane or xanthene derivatives and the triphenylmethane or phenylxanthene derivatives. The latter series differs from the triphenylmethane dyes without pyrone rings in being less easily decolorised by reduction. Conversely the leuco-derivatives are more readily oxidised by air. In these respects the pyrone dyes behave more like *ortho-* than *para*-quinonoid colours. For instance, fast acid blue shows this resemblance to an orthoquinonoid dye in a marked degree.[66]

Dialkylamino-*o*-hydroxybenzoylbenzoic acids condense with pyrogallol to form pyrone dyes of the phenylxanthene series.



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[63] Schmidlin and M. Fischer, U.S. Pat. 1219166; *J.*, 1917, 500.

[64] *British Med. J.*, 1917, Jan. 20, *Pharm. J.*, 1917, **98**, 73; *J.*, 1917, 161; *cf.* *J.*, 1912, 678.

[65] Hüssy and Hartmann, U.S. Pat. 1227624, 1228926; *J.*, 1917, 867, 905.

[66] *J. Soc. Dyers and Col.*, 1917, **33**, 78.

A more complex colouring matter is obtained giving fast greenish olive on a chrome mordant by heating this pyrone dye with *as*-dimethyl- or *as*-diethyl-*p*-phenylenediamine.[67]

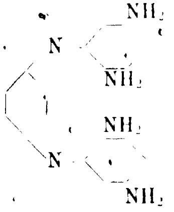
Dyes Produced by the Oxidation of Aromatic Amines

The oxidation of aniline and its homologues is facilitated by the use of small quantities of metallic salts acting catalytically. Among the salts already used for this purpose are those of copper, iron arsenic, and vanadium. It has now been demonstrated that molybdates are effective in bringing about these oxidations. This catalytic action may be manifested either at high temperatures or in warm aqueous solutions

A mixture of aniline and *p*-nitroaniline hydrochlorides, nitrobenzene, and a small amount of ammonium molybdate is boiled and the temperature raised to 220–230° C. The resulting paste dissolves in water and the red dye which is precipitated by sodium carbonate is applied in a bath of dilute acetic acid

Unmordanted cotton, wool or silk is dyed in black or dark blue shades by padding at 70° C with a mixture of *o*- or *p*-chloroaniline, hydrochloric acid, diphenylamine, potassium bichromate, potassium chlorate, and a small amount of ammonium molybdate, dissolved in water. The dyed material is afterwards put through dilute caustic soda.[68]

The reaction taking place between *p*-phenylenediamine (ursol) and hydrogen peroxide in the formation of a hair dye has been systematically studied[69] The best defined product is the tetraminodiphenyl-*p*-azophenylene of Bandrowski.



The yield of this product was always short of the calculated amount, even after three months. After removing Bandrowski's base, the unaltered *p*-phenylenediamine was estimated as *p*-benzoquinonedichloroimide by precipitation with excess of calcium hypochlorite solution

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[67] Durand, Huguenin and Co, Eng. Pat. 10732/1912 and 110042 and Ger Pat 297447; *J.*, 1916, 1214; 1917, 1174

[68] de Nagy, King, and Odell Eng. Pat. 16203 of 1915; *J.*, 1917, 78.

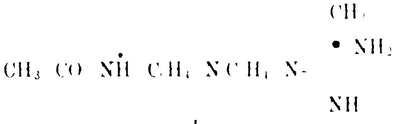
[69] Heiduschka and Goldstein, *Arch. Pharm*, 1916, **254**, 584, *J.*, 1917, 1002

By oxidising *p*-phenylenediamine in ammoniacal solution with potassium ferricyanide the foregoing oxidation product can be obtained almost quantitatively.

Potassium persulphate in cold neutral solution oxidises aniline to aniline black and *o*-toluidine to *o*-toluidine black. Acetanilide and benzanilide, when heated with concentrated aqueous persulphate, yield *p*-benzoquinone, the acyl group being liberated in the form of the corresponding acid.[70]

INDAMINE AND AZINE DYES.

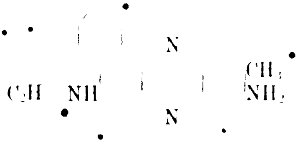
The introduction of acyl groups into indamines of the type of tolylene blue increases their fastness to washing but not to acids or to light.[71] The hydrochloride of an indamine of this type is produced by condensing 4-*p*-nitroso-1·4-acetylaminodiphenylamine with 2·4-tolylenediamine:



$$CH_3\cdot CO\cdot NH\cdot C_6H_4\cdot N C_6H_4\cdot N\text{-}\begin{matrix}CH_3\\ NH_2\\ NH\end{matrix}$$

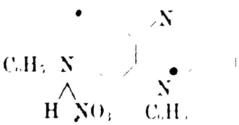
I.

With *p*-nitrosoethyl-α-naphthylamine and 2·4-tolylenediamine an azine (II) is produced:



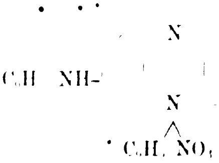
II.

Ψ-Mauveine prepared by oxidising a mixture of *p*-phenylenediamine and diphenyl-*m*-phenylenediamine, is converted into the dye, phenylaposafranine, III or IIIa, by eliminating its amino-group through the agency of the diazo-reaction:



III.

or



IIIA.

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[70] Datta and Sen, *J. Amer. Chem. Soc.*, 1917, **39**, 747; *J.*, 1917, 567.

[71] Kehrmann, *Ber.*, 1917, **50**, 554; *J.*, 1917, 639.

AZO-DYES.

Research in colour chemistry is still largely concentrated on the production of new and improved azo-dyes.

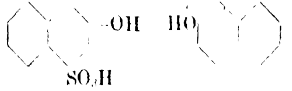
An added stimulus to the production of azo-dyes capable of forming lakes with metallic mordants is afforded by modern views on residual affinity and co-ordinated compounds to which reference was made last year.[72]

o-Dihydroxyazo Dyes and their Metallic Derivatives.

Azo-dyes containing two hydroxyl groups in positions contiguous to the azo-complex have the orientation required for the production of co-ordinated metallic salts in which the metallic atom replaces the hydrogen of one hydroxyl group through the agency of its principal valency, while its residual affinity leads to co-ordination with the neighbouring hydroxyl group, and the setting up of a cyclic complex in which the metallic atom and the azo-group are both involved.

In addition to the copper and chromium lakes already described in last year's report, the range of metals has been increased by the inclusion of nickel, cobalt, iron, aluminium, vanadium, and uranium. The tints produced on dyeing with the salts of these metals from an acid bath differ from the shades obtained from the free azo-acids. These tints can also be developed by processes applicable for chrome mordanted dyes.[73]

The chromium lakes[74] of sulphonated dihydroxyazo-dyes are obtained by heating these azo-derivatives with a solution of alkali chromite. The chromium compound of 4-sulpho-1-hydroxynaphthaleneazo-β-naphthol (I) gives fast bright blue shades on wool and silk. The azo-derivative (II) of chromotropic acid gives similar tints. *o*-Hydroxyazo-derivatives of 1-acyl-3-methylpyrazolones and cresotic acid furnish chromium salts giving red and orange shades respectively.



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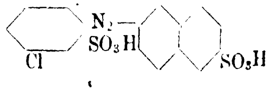

II

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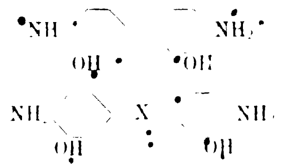
[72] *Ann Rep*, I, 1916, 85.

[73] Eng. Pat 16803, 16916/1915; *J*, 1917, 78.

[74] Engi, Straub, and Grob, Soc Chem Ind Basle, U.S. Pat 1221849; *J.*, 1917, 542.

These chromic salts show their co-ordinated character by their stability in the presence of strong alkalis. Azo-compounds having the requisite constitution are obtained by coupling with 2 molecules of 6-amino-α-naphthol-3-sulphonic acid (J acid) or a derivative, or with one molecule of this acid or a derivative and one molecule of any other coupling intermediate, the following diamines

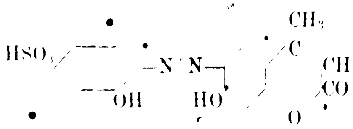


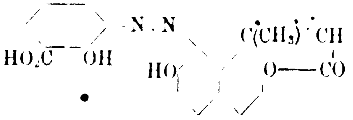
In the latter formula X[75] is one of the following bivalent groups, CH_2, CO, or NH CO NH.[76]

The resulting dyes have, in addition to their mordant-forming capacity, the property of dyeing directly on cotton

Mordant azo dyes, capable of being afterchromed and of giving soluble metallic compounds with copper and other metals, are obtained by coupling an *o* hydroxydiazo-compound or a diazonium carboxylate with the condensation product of a dihydric phenol (resorcinol or a dihydroxynaphthalene) and an alkyl β-keto-carboxylate, such as ethyl acetoacetate or ethyl oxaloacetate[77]

The following dyes are derived respectively from the methylcoumarinyl derivatives of resorcinol and 2.7-dihydroxynaphthalene respectively.





Palatine chrome black 6B has been the subject of a systematic research by I. Tomioka, who, after preparing 1-amino-2-naphthol-4-sulphonic acid by several methods, has diazotised it with sodium nitrite, zinc chloride, and subsequent addition of acetic acid. The diazo-oxide was then coupled with β-naphthol:

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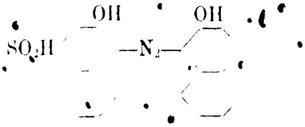
[75] Soc. Chem Ind. Basle, Eng. Pat 102881 ; *J*., 1917, 210.

[76] Eng Pat. 102881, 103251/1916 ; *J*, 1917, 210.

[77] Soc Chem. Ind. Basle, Eng. Pat. 110066 ; *J*, 1917, 1174



This research is of interest as illustrating the practical difficulties of diazotising easily oxidisable o-aminonaphthols, and of coupling the resulting internal diazo-oxide with β-naphthol.[78]

The diazo-oxide from the industrially important 2-aminophenol-4-sulphonic acid is a very soluble substance giving an intensely yellow solution. It is rarely liberated from this solution when utilised in forming chromed black dyes. Its isolation in a state of purity is facilitated by the use of purified liquid nitrous anhydride added to a cold concentrated solution of 2-aminophenol-4-sulphonic acid containing some of this acid in suspension. This method of diazotisation is applicable to the isolation of other orthodiazo-oxides soluble in water.[79]

A study of 1.5-dihydroxynaphthalene has led to the discovery of several interesting properties regarding this industrially important naphthalene derivative. 5-Methoxy-α-naphthol, formed by partial methylation with dimethyl sulphate and alkali, gives an ortho-isonitroso derivative, 5-methoxy-1.2-naphthaquinoneoxime; it also yields mono- and dis-azo dyes, the diazo-groups passing successively into positions 4 and 2.[80]

This investigation[81] of 1.5-dihydroxynaphthalene has thrown light on the constitution of the important chromed azo dye, diamond black PV. The dihydroxy-derivative contains two reactive positions, 2 and 4. It only forms a mononitroso-compound in which the nitroso-group enters position 2. Diazonium salts yield only monoazo-derivatives, in which the azo-group becomes attached at position 4. This orientation is confirmed by reducing the nitroso- and azo-derivatives, which give rise respectively to 2-amino- and 4-amino-1.5-dihydroxynaphthalene.

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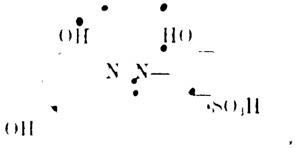
[78] *J. Chem. Ind. Tokyo*, 1917, **29**, 577; *J.*, 1917, 1043.

[79] Morgan and Tomlins, *Chem. Soc. Trans.*, 1917, **111**, 497.

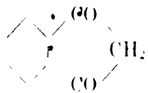
[80] O. Fischer and Hammerschied, *J. pr. Chem.*, 1917, [II], **95**, 17.

[81] Otto Fischer and Baur, *J. pr. Chem.*, 1917, [II], **95**, 261.

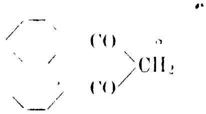
The *o*-diazo-oxides behave differently to the diazonium salts, and on coupling with 1 5-dihydroxynaphthalene furnish ortho-azo-derivatives with the azo-group in position 2 Diazotised *o*-aminophenol and 1.5-dihydroxynaphthalene give 2′-hydroxybenzene-2-azo-1 5-dihydroxynaphthalene This azo-compound and diamond black P V both furnish 2-amino-1 5-dihydroxynaphthalene Hence diamond black P.V. is the chrome lake of 1 5 dihydroxynaphthalene-2-azo-2′-phenol-5′-sulphonic acid



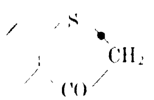
The copper salts of hydroxyazo dyes manifest co-ordinated characters similar to the corresponding chromic compounds, and increasing attention is now being paid to the application of such copper derivatives in dyeing The production of these compounds is not restricted to homocyclic intermediates An interesting series of stable copper salts has been produced from aromatic diazo-oxides and heterocyclic compounds containing the reactive group $CH_2 \cdot CO$ The following types of heterocyclic intermediates have been utilised [12]



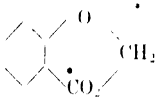
diketohydrindene



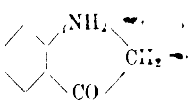
*peri*napthindandione



3-oxy-1-thionaphthene



ketocumarane



Indoxyl

The copper salt of a hydroxyazo-derivative of oxythionaphthene is obtained by coupling this cyclic ketone with 1-diazo-2-oxynaphthalene-4-sulphonic acid,

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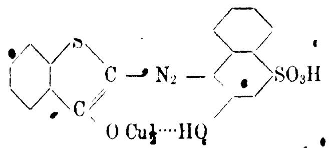
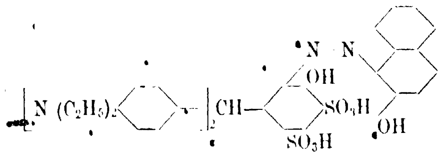
[12] Wuth and Jagerspacher, Soc. Chem Ind Basle, U S. Pat. 1233433, Eng Pat 12249, 1916; *J*, 1916, 922



and treating the azo-dye successively with copper sulphate and sodium carbonate. Whereas the azo-dye itself gives only red shades on wool, the copper salt gives violet blue shades from an acid bath, fast to washing, alkali, or light. The co-ordinated copper dye (acid salt) probably has the foregoing constitution. The copper in these compounds is not precipitated by caustic soda or ammonia.

Azo-Dyes of the Triphenylmethane Series.

An ingenious combination of the azo and triphenylmethane series of dyes has been brought about by diazotising the leuco-derivative of amino-patent blue and coupling the diazonium salt with β-naphthol, 1-phenyl-3-methyl-5-pyrazolone, or acetoacetanilide, or other intermediates giving *o*-dihydroxy-azo-dyes. The products dye wool in greenish shades, and furnish valuable chromic and cupric salts, the former giving fast green dyeings, whereas the latter produce blue shades with the β-naphthol compound (I) and greens with the β-diketo-derivatives (II) On the fibre these co-ordinated salts are very fast to light and washing. The copper compounds can be isolated and used in wool dyeing.



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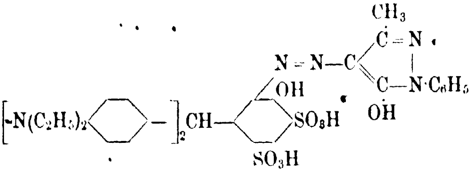


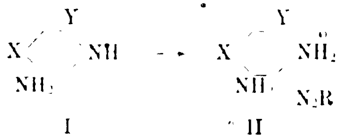
II

These triphenylmethane-azo-dyes come into the category of *o*-dihydroxy-azo-colouring matters, and as such give rise to stable metallic lakes dyeing in distinctive shades. The required configuration is arrived at by two distinct methods, in addition to the foregoing process from diazotised *o*-aminohydroxytriphenylmethane derivatives.[83]

These alternative methods are: (1) the coupling of an aromatic *o*-diazo-oxide with a hydroxytriarylmethane, derived from a reactive phenol, and a diarylhydrole containing secondary or tertiary amino-groups or hydroxyl and carboxyl groups; (2) the azo-compound from an *o*-diazo-oxide and a phenol is condensed with a diarylhydrole containing secondary or tertiary amino-groups or hydroxyl and carboxyl groups.[84]

o-Aminohydroxyazo-Dyes and their Chromic Lakes

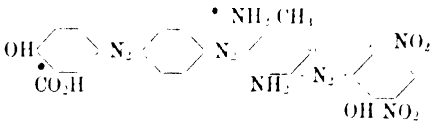
In 1902, the writer[85] showed that *m*-diamines (I) substituted in the reactive positions X and Y still retained the property of coupling with diazonium salts RN_2Cl to give rise to azo-derivatives of the general type II:



I II

These azo-derivatives containing the azo-group ortho to both amino-radicals gave yellower dyeings than those in which the azo-complex is in ortho-para-position with respect to the amino-groups.

This possibility of obtaining an azo-coupling from a *m*-diamine substituted in the ortho-para-positions X and Y has been utilised in the production of a khaki dye (III), giving with chrome mordants yellower shades than metachrome brown B.[86] The latter dye (diazotised picramic acid on *m*-tolylenediamine) is coupled with the diazo-derivative of *p*-aminobenzeneazosalicylic acid. The resulting [illegible]azo-dye (III) probably has the constitution:



III

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[83] Funcke and Jagerspacher Soc. Chem Ind. Basle, U S Pats 1237192, 1237193, J, 1917, 1002

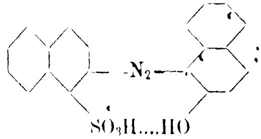
[84] Soc. Chem. Ind. Basle, Eng Pat. 104743, J, 1917, 500

[85] *Chem. Soc. Trans* 1902, 81, 86

[86] E. F. Ehrhardt and H. W. Ehrhardt, Eng Pat 108613, J, 1917, 1043

Azo-Pigments.

Closely connected with the subject of mordanted hydroxy-azo-dyes is the problem of producing azo-pigments of suitable brilliancy and durability. Certain of the most successful azo-pigments have chemical constitutions suggesting the probability of co-ordination complexes. Lithol red (I) contains its hydroxyl and sulphonic groups contiguous to the azo-chromophor. A metallic atom would replace the hydrogen atom of the more acidic sulphonic group, and then co-ordinate with the adjacent hydroxyl-group to form a cyclic metallic complex.



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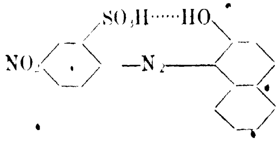
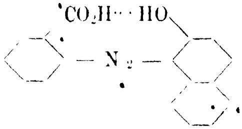


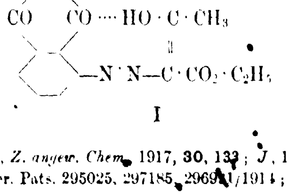
II

A similar arrangement of substituents is noticeable in the pigment lake red P (II), and in the pigment scarlet 3 B (III), where the carboxyl group becomes involved in the co-ordination complex.[87]



III

An interesting group of azo-pigments is based on the employment of 1-aminoanthraquinone. This base diazotised and coupled with ethyl acetoacetate in the presence or absence of substrata (co-precipitated compounds) gives rise to a yellow pigment (I) suitable for lake formation, insoluble in water, oil, or alcohol, and very fast to light.[88]



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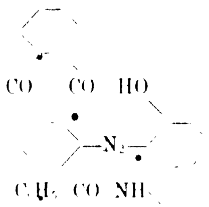
[87] O Baudisch, *Z. angew. Chem.*, 1917, **30**, 133; *J.*, 1917, 705

[88] B A S F, Ger. Pats. 295025, 297185, 2969[illegible]1/1914; *J.*, 1917, 78, 592, 639

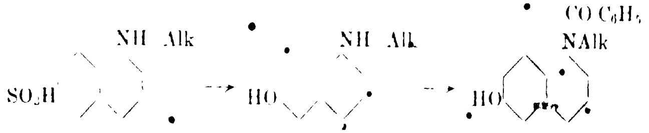
The essential groups in these pigments are the carboxyl and hydroxyl radicals in proximity to the azo-chromophor. The carbethoxyl group $CO_2 \cdot C_2H_5$ may be replaced by $CO \cdot NHR$ where R is an aromatic nucleus.

Bright red azo-pigments (II) are produced[84] by coupling anthraquinone-1-diazonium chloride with 8-benzoylamino-β-naphthol or its derivatives substituted in the benzoyl group, with or without Turkey red oil and in the presence or absence of substrata. These red pigments are insoluble in oil or water, are not affected by alcohol or calcium hydroxide, and are remarkably fast to light.



II

The benzoylamino-group $C_6H_5 \cdot CO \cdot NH$ may be alkylated to $C_6H_5 \cdot CO \cdot N(CH_3)$, giving rise to similar red pigments. In the latter case the sulphonic acids (III) of alkyl-α-naphthylamines are used as intermediate compounds, being converted by caustic fusion into naphthol derivatives (IV), and these products benzoylated in the alkylamino group (V).



III IV V

Azo-Dyes for Wool.

The industrially important γ- or G-acid (2-amino-8-hydroxynaphthalene-6-sulphonic acid) is utilised in the production of red azo-dyes by coupling in acid solution with diazotised acylated *m*-phenylenediaminesulphonic acids, the free azo-sulphonic acid having the following formula:[85]

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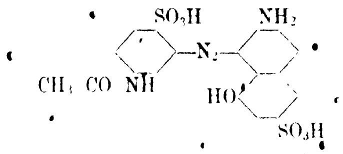
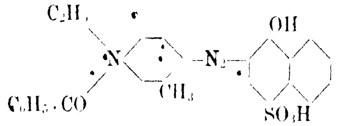
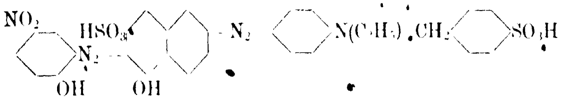
[84] Bergdolt and Synthetic Patents Co., U.S. Pat. 1201544; *J.*, 1916, 1214.



Acylated derivatives of *p*-phenylenediamine have been employed in a similar manner, the following product with α-naphthol-4-sulphonic acid (N.W.) giving on wool bright scarlet red shades, fast to fulling :[90]



In addition to its employment as a component of direct cotton dyes, J acid (2-amino-5-hydroxynaphthalene-7-sulphonic acid) has been utilised in producing wool dyes amenable to after-chroming. The suitable contiguity of hydroxyl-groups is secured by coupling J acid in alkaline solution with an *o*-diazo-oxide. The resulting *o*-dihydroxyazo-derivative is then diazotised and coupled with ethylbenzylaniline-4-sulphonic acid or a homologue. The free sulphonic acid of the final disazo-dye has the following constitution :—[91]



In this coupling, other *o*-diazo-oxides may replace the one from 2-amino-4-nitrophenol.

Wool dyes ranging from yellowish orange to bluish red are produced by coupling the bisdiazonium salts of 3 3′-diaminodiphenylmethane and its homologues with 2 molecular proportions of intermediate azo-component, of which one molecule is a naphtholsulphonic acid.

3.3′-Diamino-4.4′-dimethyldiphenylmethane is bisdiazotised, and coupled successively with 1-(4′-sulpho-)-phenyl-3-methyl-5-pyrazolone (in aqueous sodium acetate) and α-naphthol-4-sulphonic acid (in aqueous sodium carbonate). The disazo-dye

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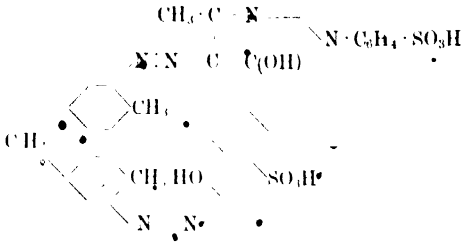
[90] Hauptmann and Synthetic Patents, Co , U S. Pat. 1199890 ; *J.*, 1916, 1151.

[91] Schöner, Akt.-Ges. f. Anilinfabr., U.S Pat 1[illegible]3075 ; *J*, 1917, 334.



gives reddish-orange tints on wool, fast to light and washing.[92]

Developed Azo-Colours.

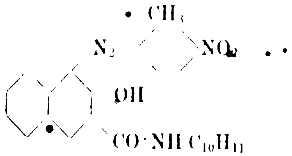
Considerable attention is still being devoted to the production of colour on the fibre by the formation of insoluble azo-pigments.

The acylamides of 2-hydroxy-3-naphthoic acid are greatly in request as suitable coupling agents. They are produced by the following methods:

(1) A mixture of 2-hydroxy-3-naphthoic acid and excess of aromatic amine is treated with phosphorus pentachloride. The acid chloride first formed reacts with the aromatic amine to furnish the corresponding acylamide in quantitative yield.[93] The amide and *p*-toluidide are obtained by employing the corresponding bases in this condensation.

(2) An O-acylated 2-hydroxy-3-naphthoic acid is heated until an anhydro-derivative is produced. This intermediate compound on treatment with ammonia or an amine yields the corresponding amide.[94]

The tetrahydro-α-naphthalide of 2-hydroxy-3-naphthoic acid gives rise to red azo-pigments.[95]



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[92] Anderwert and Schobel, Soc Chem Ind Basle, U S Pat. 1233742; *J*, 1917, 1002.

[93] M. L. and B, Ger. Pat. 294799; *J.*, 1917, 286.

[94] M. L. and B, Ger. Pat. 295183; *J*, 1917, 286

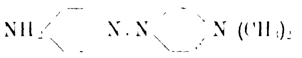
[95] List and Synthetic Patents Co., U.S. Pat. 1215359; *J*, 1917, 382.

An interesting development in the art of producing insoluble azo-colours on the fibre arises from the discovery that certain of the intermediates employed in coupling with diazonium salts have considerable affinity for the textile fibres.

Among these mordanting intermediates are the acyl derivatives produced by condensing 2-hydroxy-3-naphthoic halides or their O-acetyl derivatives with 2-amino-5-naphthol-7-sulphonic acid (J acid). The product, 2′-hydroxy-3′-naphthoyl-2-amino-5-naphthol-7-sulphonic acid, which gives in alkaline solution the typical yellow colour of the alkali salt of an arylamino-derivative of 2-hydroxy-3-naphthoic acid, is absorbed by cotton from alkaline solutions and by silk from dilute acetic acid solutions. It combines on the fibre with 2 molecular proportions of diazonium salts, and in this way useful dyeings fast to washing are obtained.[96]

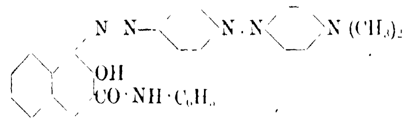
An important group of developed dyes giving fast black shades on cotton and linen is obtained by making use of *p*-amino-azo-compounds having the general formula $NH_2.R.N_2.R.N.(Alk)_2$. These compounds are obtained by coupling with tertiary amines, $R.N.(Alk)_2$, either (I) nitro aromatic amines, $NO_2.RNH_2$, or acyl-*p*-diamines, $NHAc.R.NH_2$. In the former case the required *p*-amino-azo compound (I) is obtained by Meldola's method of reducing the nitro-group. In the latter case this result (I) is produced by removing the acyl group by hydrolysis.

The simplest example of this group is the developed dye (II) produced by diazotising 4-dimethylamino-4′-*p*-aminoazobenzene (I).



I

and by coupling its diazo-derivative with the anilide of 2-hydroxy-3-naphthoic acid.[97]



II

The dyeing may be varied by using more complex arylides of this hydroxynaphthoic acid, and by starting with the homologues and derivatives of the foregoing aminoazo-derivative (I). The tertiary amine may be dimethyl-*m*-toluidine, dimethyl-α-naphthylamine or their homologues. The coupling bases may be 5-nitro-*o*-toluidine, 5-nitro-*o*-anisidine, or similarly constituted acylated *p*-diamines.[98]

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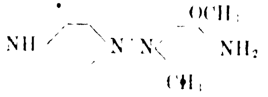
[96] Griesheim-Elektron, Ger. Pat. 2957[illegible]; *J.*, 1917, 542.

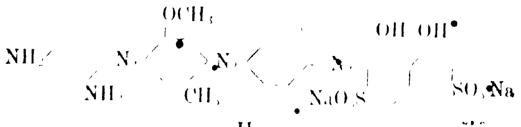
Direct Cotton Azo-Dyes

Direct cotton salt dyes having the property of developing on the fibre intense shades of black on subsequent treatment with diazo compounds are obtained by coupling the bisdiazonium salt of 4.4′-diaminoazobenzene or its homologues with one molecular proportion of chromotropic acid (1.8-dihydroxynaphthalene-3.6-disulphonic acid), and one molecular proportion of *m*-phenylenediamine. The azo-compound made by coupling *p*-nitroaniline with *p*-cresidine (3-amino-4-methoxy-1-methylbenzene) leads on mild reduction to the intermediate diaminoazo compound (I),



I

which on bisdiazotisation, and coupling with the foregoing intermediates furnishes the trisazo-dye (II), giving violet shades on cotton.



II

Black shades are developed by the further action on this salt dye of *p*-nitrobenzenediazonium chloride.[99]

The production of direct cotton azo dyes from J acid is exemplified by a series of tetrakis-azo-derivatives in which this aminonaphthol-sulphonic acid (in alkaline solution) is the penultimate component and resorcinol the final component. As an example of this group the following dye may be formulated :—

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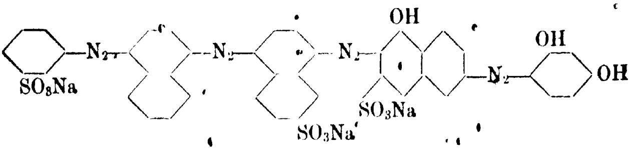
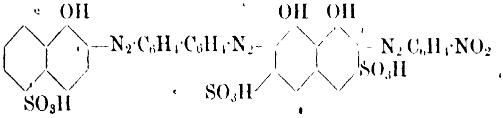
[98] This patent contains a recipe for producing these developed azo-pigments on the textile fibres.

[99] Haugwitz and Akt.-Ges. f. Anilinfabr., U.S. Pat. 1260154; *J.*, 1917, 211.



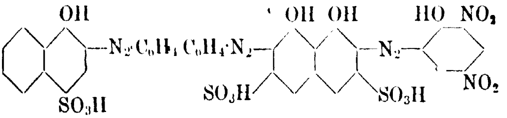
This dye and its analogues furnish blue shades on cotton, which, owing to the presence of the resorcinol complex, are increased in fastness to light and washing by subsequent treatment with formaldehyde.[100]

A group of trisazo-dyes, having the valuable property of dyeing both cotton and wool directly, is obtained by an application of chromotropic acid (1.8-dihydroxynaphthalene-3.6-disulphonic acid). This acid is first coupled with diazotised *p*-nitroaniline (or *p*-aminophenylglycine), and the monoazo intermediate is then coupled with bisdiazotised benzidine. The second disazo intermediate which still contains a diazo-group is then coupled with α-naphthol-5-sulphonic acid to yield the trisazo-dye I. This dye gives a blue tint on unmordanted cotton (sodium sulphate bath), and brown to black shades on wool (acid sodium sulphate bath). A similar dye (II) is produced by coupling chromotropic acid successively with diphenylbisdiazonium chloride and diazotised picramic acid, and combining the resulting diazo-disazo intermediate with α-naphthol-4-sulphonic acid.



I

These trisazo-dyes when on woollen goods are improved by after-chroming.[101]



II

The marked influence of the unsaturated styryl-group in deepening the colour and increasing the affinity for cotton of the azo-dyes made from mono- and di-aminostyrylbenziminazole bases is the subject of a research by Kym and Jurkowski.[102] These bases diazotised and coupled with β-naphthol-3.6-disulphonic acid give direct azo colouring matters dyeing cotton in intense reddish violet shades. The azo-dyes from the corresponding aminophenylbenziminazoles yield only light violet or lilac shades.

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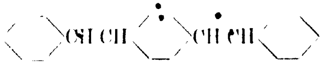
[100] Akt.-Ges. f. Anilinf., Eng. Pat. 104967; *J.*, 1917, 1174.

[101] Stebbins, U.S. Pat. 1235253; *J.*, 1917, 1043.

The styryl group is a typical auxochrome displacing the ultra-violet fluorescence into the visible spectrum.

p-Distyrylbenzene, prepared from terephthalic aldehyde and magnesium benzyl chloride, is a coloured hydrocarbon with very powerful fluorescent properties.[103]

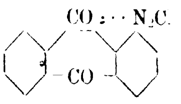


The Diazo-Reaction

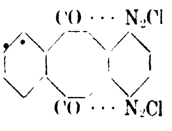
The utilisation of amino-derivatives of anthraquinone in the production of azo-pigments lends additional interest to a recent study of the diazo-derivatives of these amines

The diazonium salts of the anthraquinone series are remarkable on account of their comparative stability. Anthraquinone-1-diazonium chloride (I) dissolves unchanged in boiling water and crystallises therefrom on the addition of sodium chloride solution. The *p*-chloro-derivative of this diazonium salt is also very stable. Anthraquinone-1.4-bisdiazonium chloride (II) can also be salted out from its solution in boiling water. Anthraquinone-2-diazonium salts are less stable.

These properties suggest that the carbonyl groups of anthraquinone have a stabilising influence on contiguous diazonium groups, since the foregoing stable diazonium salts all contain the diazonium and carbonyl radicals in close proximity.[104]



I.



II.

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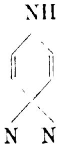
[102] *Ber*, 1916, **49**, 2681; *J.*, 1917, 209.

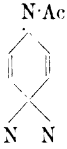
[103] Kauffmann, *Ber.*, 1917, **50**, 515; *J.*, 1917, 706.

[104] A. Schaarschmidt, *Ber.*, 1916, **49**, 2678; *J.*, 1917, 209

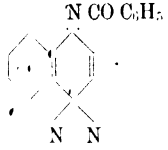
Another step nearer to the isolation of the hypothetical *p*-diazoiminobenzene (I) has been reached by the production of its simplest acyl derivatives (II)



I.



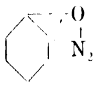
II.



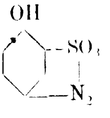
III.

The formyl and acetyl derivatives, prepared by adding liquid nitrous anhydride and ether successively to an acetone solution of formyl-*p*-phenylenediamine and acetyl-*p*-phenylenediamine respectively, are pale yellow compounds evolving nitrogen slowly at the ordinary temperature, and passing into ill-defined resinous products. The benzoyl derivative, similarly prepared, is stable under atmospheric conditions, and so also is the benzoyl derivative (III) of *p*-diazoiminonaphthalene.[106] These diazoimides all couple additively to form azo-compounds with phenols, naphthols, and reactive aromatic bases, such as the naphthylamines and *m*-phenylenediamine and its homologues.

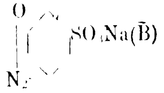
A comparative study of the diazo-derivatives of the sulphonic acids of the *o*-, *m*-, and *p*-aminophenols showed that the *o*-diazosulphonic acid and its salts had the internal *o*-diazo-oxide structure (I).



I.—Yellow *o*-diazo-oxide.



II.—Colourless diazonium suphonate.



III.—Yellow *p*-diazo-oxide.

The *p*-diazosulphonic acid is in reality an internal diazonium sulphonate (II). When neutralised with alkalis or bases this substance gave yellow salts probably possessing the *p*-diazo-oxide configuration (III). Stable yellow salts were obtained with the bases piperidine, dibenzylamine, and brucine.

The meta-diazosulphonic acid is also an internal diazonium sulphonate (IV),

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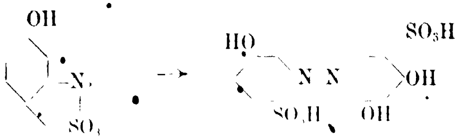
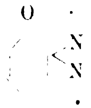
[106] Morgan and Upton, *Chem. Soc. Trans.*, 1917, **111**, 187; *J.*, 1917, 449.

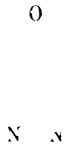


IV V

but this compound shows no disposition to yield an internal metal diazo-oxide, and when treated with alkalis or bases, especially ammonia, it loses half its diazo-nitrogen and passes into a yellow azo dye (V).[106] Other investigators have also attempted without success to obtain the internal *m*-diazo-oxides. The non-existence of these meta compounds suggests an alternative quinonoid constitution for the *o*- and *p*-diazo-oxides (VI and VII).



VI



VII.

Chromic Salts of Mordant Dyes

An ingenious process[107] of producing the soluble chromium salts of acidic dyes is achieved by producing a soluble solution of a chromic compound and then treating this substance with a mordant-forming dye. Sodium chromate is heated with glucose solution at 80°–90° C. until the chromium is reduced to the tervalent condition. The alkaline solution is neutralised with acetic acid, and treated with alizarin blue paste or other similar mordant dye. The resulting soluble chromic salt is utilisable directly in the dye bath; its co-ordinated character is manifested by its resistance to the action of aqueous alkalis.

VAT DYES

Considerable activity is still being manifested in researches on the vat dyes. These investigations deal either with the improvement of known dyes, or the discovery of new colouring matters amenable to the vat process.

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[106] **Morgan and Tomlins,** *Chem. Soc. Trans.*, 1917, **111**, 497; *J.*, 1917, 866.

[107] **Dreyfus and Beckers Aniline and Chemical Works,** U.S. Pat. 1228089; *J.*, 1917, 867.

Indigo.

The shortage in the supply of indigo, which existed from the outbreak of war until the latter part of 1916, has stimulated in a very marked degree the cultivation of the indigo plant. In British India the total area under indigo in 1916–17 was 756,400 acres, being 114% in excess of the acreage of the preceding year. The corresponding increase in the total yield of indigo was 73%. In 1915 the amount of natural indigo imported into the United Kingdom was 25 157 cwts., whereas in 10 months of 1916 the import was 28,245 cwts., the latter is practically equal to the largest annual amount of synthetic indigo imported into the United Kingdom during the period 1911–15, the maximum being 28,302 cwts. for the year 1912. This increase in the cultivation of the indigo plant is being accompanied by a systematic and scientific inquiry into the agricultural conditions affecting the growth of the plant, and the formation of indican. Not less important in the production of natural indigo is the part played by the bacteria in the steeping vats. Numerous species of bacteria have been isolated and certain of these species have been classified as beneficial or harmful. This investigation raises the hope that an improvement in the formation of natural indigo may be brought about by controlling the bacterial fermentation in the vat.[108]

These important additions to the supply of natural indigo, coupled with the extremely favourable output of synthetic indigo LL from the Ellesmere Port works, should serve to make the British Empire self-contained as regards this important vat dye.

The conditions favouring the formation of indigo from indican-containing varieties of indigo plants cultivated in Formosa have been studied. The optimum temperature for the hydrolysis of indican is 50° C., no indigo being produced at 80° C. At 69–70° the indigo red content is greater than when steeping is carried out at 40°–50° C.

The foregoing activities serve to indicate that the struggle between natural and synthetic indigo has not ended finally in favour of the latter. Improvements in the cultivation and production of the former are evidently quite practicable. On the other hand the possibility of improving on the existing synthetic processes is not excluded and several researches on these lines are now in progress.[109]

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[108] A. and G. L. Howard, *Bull. No. 67, Agric. Res. Inst. Pusa*; *J.*, 1917, 130; D. T. Reid, *Agric. J. India*, 1917, 12, 1; *J.*, 1917, 333.

[109] *cf.* Cone, U.S. Pat. 1211413; *J.*, 1917, 211.

Indanthrene Vat Dyes

The chlorination of indanthrene blue greatly increases the fastness of this dihydroazine derivative to light and to the action of hypochlorite. Brighter shades of blue are also obtainable by this substitution.

The tri- and tetra-chloro-derivatives prepared by the action of chlorine in excess at temperatures not greatly exceeding 40° C. on indanthrene suspended in an inert organic liquid are characterised by the foregoing properties.[110]

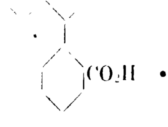
The dichloroindanthrene resulting from the action of sulphur chloride on indanthrene suspended in an inert liquid at a temperature below 100° C. is faster to light than the brand known as indanthrene blue GCD (dichloroindanthrene), and nearly as fast as indanthrene blue GC (dibromoindanthrene). The new product is also suitable for the manufacture of light blue pigments.[111]

Leuco-indanthrene precipitated by acidifying an indanthrene vat is oxidised, yielding indanthrene blue in a very finely divided form, suitable for the manufacture of pigments.[112]

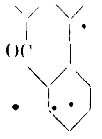
Sulphur dyes of the vat series are produced by heating anthraquinone or anthranol with alkali thiosulphates. The products are insoluble in water, or aqueous alkalis or alkali sulphide. When reduced in an alkaline vat these thionated products yield soluble leuco derivatives, dyeing cotton in olive to olive brown shades fast to chlorine.[113]

Benzanthrone

A new synthesis[114] of benzanthrone derivatives has been accomplished, the starting point being 1-phenylnaphthalene-2 3-dicarboxylic acid (I)



I.



II.

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[110] M., L. and B., Ger. Pat. 296841; J., 1917, 591.

[111] Chem. Fabr. Griesheim-Elektron, Ger. Pat. 296192; J., 1917, 591.

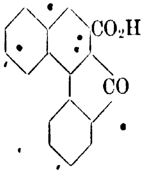
[112] M., L. and B., Ger. Pat. 294830; J., 1917, 78.

[113] R. Wedekind and Co., Ger. Pat. 297080, *cf.* Ger. Pat. 296207; J., 1917, 639, and Eng. Pat. 19435/1913.

[114] Schaarschmidt, *Ber.*, 1917, **50**, 294; J., 1917, 591.

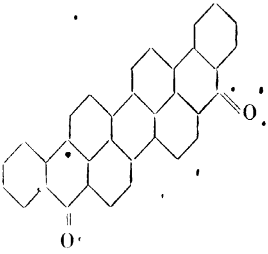
This acid yields benzanthronecarboxylic acid (II) on treatment with concentrated sulphuric acid, or on warming its benzene solution with phosphorus pentachloride, the residue, after removing the solvent, being treated with aluminium chloride.

Both these acids on condensation with benzene and aluminium chloride give rise to benzoylbenzanthrone. Monobromophenylnaphthalene-2 3-dicarboxylic acid condenses in a similar manner to yield bromobenzoylbenzanthrone. In preparing 1-phenylnaphthalene-2′.3-dicarboxylic acid by alkali fusion of allochrysoketonecarboxylic acid (III): -



III.

it was found that a small amount of bluish violet vat dye was produced, which is probably dibenzanthrone (IV).



IV

An oxidation product of this complex dibenzanthrone (IV) is heated with *p*-toluidine and boric acid. The product yields a blue hydrosulphite vat, from which cotton is dyed in olive-green shades of great fastness to soap or chlorine.[115]

The base is employed only as a condensing medium, but other organic liquids of high boiling point may be used, such as nitrobenzene, naphthalene, or cresol.

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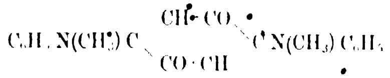
[115] Isler and B A S F., U S. Pat 1207762; *J.*, 1917, 181; *cf.* U.S. Pat. 1093427.

Benzoquinone Vat Colours.

The commercially important vat dyes having a quinonoid structure have generally so far been derivatives of anthraquinone. A significant extension of this group of dyes to derivatives of the simplest aromatic quinone, namely, *p*-benzoquinone, has recently been made known.

The *para*-quinones, when heated in a suitable organic solvent with arylaminoacetic acids, give rise to acylamino-derivatives of these quinones, which have the property of reducing to soluble leuco-derivatives in the hydrosulphite vat. These leuco-compounds have an affinity for the animal fibres.[116]

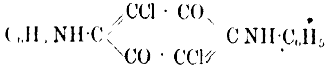
The compound from phenylglycine and *p*-benzoquinone



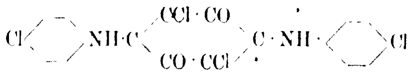
$$C_6H_5\cdot N(CH_3)\cdot C\left\langle\begin{matrix}CH\cdot CO\\CO\cdot CH\end{matrix}\right\rangle C\cdot N(CH_3)\cdot C_6H_5$$

is a brown crystalline powder sparingly soluble in the volatile organic solvents, or in aqueous acids or alkalis. In an alkaline hydrosulphite vat it gives a colourless leuco-derivative, which on oxidation yields yellow tints on the animal fibres. Dichloroquinone or chloranil can be utilised in the production of these vat dyes, the colourless leuco-derivatives of which also give yellow tints on wool.

Similar products, suitable for vat dyeing[117] are obtained by heating at 180°-200° with copper powder, or some other metal (*e.g.*, zinc-iron), the following acylamino-derivatives of halogenated benzoquinone:—



$$C_6H_5\cdot NH\cdot C\left\langle\begin{matrix}CCl\cdot CO\\CO\cdot CCl\end{matrix}\right\rangle C\cdot NH\cdot C_6H_5$$



Sulphide Dyes.

An instructive summary of our present knowledge of sulphide dyes has been compiled by Rowe.[118]

This group of dyes undoubtedly includes a section containing the thiazole nucleus present in primulin and dehydrothio-*p*-toluidine. The yellow, orange, and brown dyes derived by the action of sulphur on C-alkylated diamines of the benzene and naphthalene series probably belong to this group. The nitroamino-derivatives corresponding with these diamines are also utilisable in this condensation, but the presence of alkyl groups in the aromatic nucleus is essential in both instances, these side chains furnishing the carbon atom of the heterocyclic thiazole ring.[119] Providing that alkyl groups are present, the sulphonic or carboxylic acids of the benzene, diphenyl, or naphthalene amines (*e.g.*, ethyl-α-naphthylaminesulphonic acids) are amenable to the sulphur treatment.[120]

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[116] Homolka and M. L und B, U S Pat 1209163, *J.*, 1917, 211.

[117] Kalle und Co, U S Pat 1209212; *J*, 1917, 211.

[118] *J. Soc. Dyers and Colorists*, 1917, **33**, 9, *J* 1917, 208.

The drain on coal-tar products for high explosives has led to a search for intermediates in colour making from vegetable sources. The gums or gum resins produced from plants of the genus *Xanthorrhœa*, when treated with alkali and sulphur, or with sodium sulphide, yield sulphide colouring matters dyeing in various shades of bronze, brown-grey, or black.[121] These investigations are comparable with those of Croissant and Brétonnière, who more than 40 years ago subjected a very large and heterogeneous group of organic waste products to the alkali sulphide fusion from which investigation, however, only one sulphur dye, namely, cachou de laval, was obtained.

More definite products containing nitrogen, as well as sulphur, are prepared by fusing with alkali sulphide, the nitro or nitroso derivatives of yacca gum (from *Xanthorrhœa arborea* or *X. hastilis*) or of Congo resin (from *Hymenæa verrucosa* or *Copaifera copallina*). The azo-derivatives of yacca gum, prepared by coupling the gum with diazonium or bisdiazonium salts in alkaline solution, can also be used in the sodium sulphide fusion.[122]

The original Vidal sulphide black was obtained by the fusion with sodium polysulphide of *p*-nitrophenol or *p*-aminophenol. The discoverer now produces a sulphide black by heating *p*-aminophenol with sulphur and resorcinol or *m*-phenylenediamine in a reflux apparatus.[123]

The residues from the manufacture of sulphide dyes contain sodium thiosulphate, which is decomposed either with warm sulphuric acid, or with an acid salt, especially sodium hydrogen sulphate. Sulphur is precipitated and recovered, and the filtrate contains crude sodium sulphate.[124]

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[119] Akt.-Ges. f. Anilinfabr., Ger. Pat. 295251; *J.*, 1917, 211.

[120] F. Bayer und Co., Ger. Pat. 295104; *J.*, 1917, 211.

[121] Miller and Irlam, Eng. Pat. 104353; *J.*, 1917, 500. *cf.* Eng. Pat. 1489 of 1873.

[122] G. H. Frank, Eng. Pat. 105118 and 105119; *J.*, 1917, 542.

[123] Vidal, Eng. Pat. 105162; *J.*, 1917, 542.

[124] Akt.-Ges. f. Anilinfabr., Ger. Pat. 295859; *J.*, 1917, 647.

This review is probably even less complete than its forerunner, because of the difficulty of obtaining information as to the trend of colour research in Germany and Austria. The volume of investigations published on dyes and their accessories in available European periodicals and patent literature is, however, remarkable, considering the distractions of the war. A striking feature of the year has been the marked increase in the patenting activities of American dye producers. It is evident that these manufacturers recognise fully the importance of research in this branch of applied chemistry.

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FIBRES, TEXTILES, CELLULOSE, AND PAPER

By J. F. Briggs, A.C.G.I.

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The period under review may be regarded in this, as in all other industries, as one of transition, characterised by two governing influences: Adaptation to the temporary stringency of war conditions and preparation for developments and replacements after the war. The withdrawal of labour and the strict Government control of all sources of supply have been disturbing influences, having both temporary and permanent results difficult to estimate. As regards industrial research and invention the conditions have been both stimulative and retarding. The scarcity of published research work of fundamental interest is rather noticeable, nevertheless a very considerable activity has been manifested in the cellulose industries, particularly in the search for substitutes for materials and products of foreign origin.

FIBRES

Cotton. J. H. Barnes[1] has made a close study of the mineral constituents of cotton lint with special reference to the alleged sophistication of certain Indian cottons by hygroscopic salts with a view to increasing weight. He concludes that such general allegations are without foundation, but points out that cotton cellulose and pectins combine with some of the constituents of saline soils, either by adsorption or chemically, in the course of growth. Further, genuine cotton fibre may contain upwards of 1% of ash constituents, and the presence of highly varying quantities of silica seems to have escaped attention hitherto.

K. H. Vakil[2] has published an important paper on cotton-seed products, dealing particularly with Indian cotton. According to statistics quoted, the recent annual production of cotton in India amounts to 800,000 tons, which is equivalent to nearly 1,870,000 tons of seeds. The Indian seed differs from the Egyptian in being covered with a fine down or "fluff" which is removable by suitable "delinting" machinery, yielding 1·0–1·5 of lint. Cotton-seed delinter fibre is therefore likely to become a valuable by-product of the oil-seed crushing industry available in fairly substantial quantities as raw material for the paper and cellulose plastic industries. At present, the seed is usually crushed with the "fluff," but as the latter readily absorbs the oil and causes heating of the mass by fermentation, its removal at an early stage would improve the storage qualities of the seed and increase the yield of oil.

One of the most troublesome impurities of cotton and linen fibres is the highly resistant vegetable protein. Many of the irregularities in chemical behaviour, generally attributed to the fat and wax, are often more properly to be sought for in the imperfect removal of the original proteins, traces of which can be detected by the "chloroamine" reaction even after several treatments with boiling alkali. B. S. Levine[3] blames these impurities for the subsequent yellowing of bleached cotton textiles and proposes to remove them by digestion with cultures of suitable bacteria. O. Rohan[4] similarly proposes to treat the raw goods with a 0·1 solution of pancreatin or other proteolytic and lipolytic enzymes and claims to dispense with the usual boiling-out treatment with alkali.

Freiberger[5] discusses the determination of so-called "wood gum," which is not a very aptly chosen expression for the complex mixture of matters extracted from raw or imperfectly bleached cotton by treatment with 5 sodium hydroxide in the cold for 24 hours. This complex extract may be separated into three fractions by the successive addition of alcohol, neutralisation by hydrochloric acid, and acidification with hydrochloric acid. The main constituents of these three fractions are respectively—alkali-soluble "cellulose," xylan or wood gum proper, and fatty acids, but the separations cannot be regarded as in any way sharp and the procedure is extremely tedious.

After cold extraction the cotton is boiled with 1 sodium hydroxide for 5 hours with exclusion of air and the addition of a little resin and dextrose, under which conditions the loss of weight of the cellulose proper does not exceed 1. The above method may be useful when it is desired to differentiate between superficially bleached, imperfectly purified cotton and cotton which has been chemically modified by excessive bleaching.

The question of the nature of hydrated cellulose is one of extreme interest as an example of the intimate relations between the chemical and physical modifications of the colloidal condition. The hydration of cotton cellulose may be produced by many chemical agencies and even by mechanical treatment in presence of water, and may be described as a condition of inter-molecular distension, whereby the surface reactions are largely increased and the "adsorption" phenomena correspondingly developed. R. Haller[6] has made some important observations on the ultramicroscopic structural differences between ordinary and mercerised cotton and has established the fact that in the latter the micellæ are more widely separated than in the original membrane and therefore penetrable by particles of larger dimensions.

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[3] *J. Ind. Eng. Chem.*, 1916, **8**, 298; *J.*, 1916, [illegible].

[4] Eng. Pat. 100,224/1916; *J.*, 1916, 1057.

[5] *Z. anal. Chem.*, 1917, **56**, 299; *J.*, 1917, 923.

A Committee has been formed in Manchester to act in conjunction with the Department of Scientific and Industrial Research, to determine the best means for encouraging research and technical education in the cotton industry.[7]

Flax, Hemp, and Jute. There are few additions to the literature relating to the standard bast fibres. S. H Higgins, following up his previous study of the chemistry of flax wax[8], in which it was shown that the wax of linen fabrics could not be advantageously attacked by boiling with soda alone, has regarded the presence of this wax as the chief *raison d'être* of the tedious preliminary lime boil and "black sour" and claims[9] that this treatment, with its attendant danger of lime stains, may be avoided by a preliminary extraction of the goods with volatile solvents, after which the soda boil may be applied direct. The flax wax thus obtained is a complex mixture from which the true hard wax may be separated by suitable purification. In times like the present the wax by-product possesses a very considerable commercial value, but it remains to be seen whether the treatment proposed is technically and economically justified.

A new process of retting bast fibres by pure cultures of bacteria, as applied to hemp, is described by G. Rossi.[10] This process, in which specific pectic bacteria, such as *B. comesii*, are employed, may mark the beginning of a new era in the industrial preparation of bast fibres and is worthy of the most serious attention. It is stated that the action of these bacteria is perfectly specific and a complete resolution of the pectic binding materials is brought about without the slightest deleterious action on the cellulose. Hemp bast tissue is rapidly resolved into its constituent elements and may be kept for years in contact with the living bacteria under aseptic conditions without appreciable weakening of the fibre structure. The process has the advantage of being an aerobic one and the deleterious organisms are suppressed by aeration. A factory is working in France with the most encouraging results and the quality of the fibre is stated to be superior to that produced by the older methods of field retting. The hemp is preferably scutched in the green state and the dried material may be stored. The fibre retted after scutching is smoother, more glossy, and less divided than ordinary hemp, but a slight brushing process suffices to impart the necessary degree of fineness.

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[6] *Kolloid Zeits.*, 1917, **20**, 127; *J.*, 1917, 923.

[7] *J.*, 1917, 440.

[8] *J.*, 1914, 902.

[9] Eng. Pat. 102,892/1916; *J.*, 1917, 211.

[10] *Bull. Agric. Intell.*, 1916, **8**, 1067; *J.*, 1917, 79.

In the case of flax plants grown for seed, J. Brohm[11] proposes to cut the heads at maturity and leave the stalks standing until a natural retting process has taken place under the action of the weather.

Miscellaneous textile fibres. Owing to the scarcity of raw materials created by the war, increased attention has been directed towards the utilisation of substitutes for standard fibres, but in this country no very striking results have been reached owing to the fact that in so far as such substitutes are of overseas origin they are just as difficult to obtain as the original article. In Germany, on the other hand, new supplies of cotton and jute have been cut off as far as possible and it has been necessary to make use of the European fibres such as flax and hemp supplemented by such substitutes as can be produced in the country. In a review of the textile substitutes which have been employed in 1916, Massot[12] refers to paper yarns, which have undergone an enormous development, and to the attempted resuscitation of the nettle fibre industry. The nettle yields 10 of fibre calculated on the green stem, and an organisation consisting of over 12,000 persons was engaged in collecting the stems. In the year 1916, 1,650 tons of dry stems was thus obtained for fibre manufacture. The stems undergo a chemical retting process in which the protein is not coagulated and are broken in the same manner as flax stems. In a recent Bulletin of the Imperial Institute[13] a sample of nettle fibre from India has been reported on. The fibre was not well prepared, having only been treated by mechanical means. The degummed fibre might be of interest for mixing with jute and hemp but cannot be regarded as a satisfactory substitute for flax or ramie from the point of view of strength and spinning qualities.

Among the minor developments in connection with new textile fibres may be mentioned patents relating to the treatment of papyrus[14] osier bark,[15] and the broom plant.[16] As a substitute for jute, *Hibiscus cannabinis* and allied plants of the order *Malvaceæ* yield fibres of very similar appearance and properties. Several samples of such fibres have been examined at the Imperial Institute[13] and found worthy of attention but inferior to jute of the first quality. According to Vournasos[17] *Hibiscus* fibre yields after bleaching a cellulose of fine staple superior in absorbent power to ordinary cotton.

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[11] U.S. Pat. 1203546; *J.*, 1917, 212.

[12] *Z. angew. Chem.*, 1917, **30**, 67; *J.*, 1917, 543.

[13] *Bull. Imp. Inst.*, 1917, **15**, 7; *J.*, 1917, 1003.

[14] Ger. Pat. 291302; *J.*, 1916, 833.

In the same Bulletin of the Imperial Institute a number of other fibres produced in the British Empire are described. Among these may be noted a fibre obtained from *Asclepias fruticosa*, widely distributed in South Africa and known locally as *Melkbosch*. This fibre is exceptionally rich in cellulose and has been suggested as a substitute for Sisal hemp, but it is very much inferior in length of staple. The same plant also yields a vegetable down of the kapok class, known as *Akund*, which is brittle and considerably inferior to genuine kapok in resilience.

Kapok.—Owing to the war, kapok has acquired a vastly increased interest as a stuffing for life-saving appliances at sea, and samples have been submitted to the Imperial Institute from the Sudan and from Togoland, in which latter colony the Germans had developed a substantial industry. C. F. Cross and E. J. Bevan[18] have contributed a very important study on kapok, dealing with its specific characteristics and commercial valuation. The value of the genuine kapok depends on its capacity of resisting the penetration of water over very prolonged periods of immersion. This property is not due to the presence of specific water-repellent constituents, since the total fat, wax, and resin contents are between the limits of 0.5–1.8%. The resistance to water is attributable to the peculiar structure of the fibre in the form of a thin-walled, resilient tube enclosing a relatively very large volume of air. When the down is immersed in a hydrocarbon liquid the tubular air is not expelled and the apparent specific gravity under these conditions is an important measure of quality, ranging from 0.404 for the best to 0.686 for the lower grades. The cell-wall is to some extent lignified, but only the inferior qualities show a strong reaction with phloroglucinol; relatively large proportions of "furfuroids" or pentosans are present, particularly in the lower grades. In this investigation the chemical type of the cell substance has not been fully elucidated and the properties of the down, particularly its remarkable resilience, are not completely explained on the basis of physical structure alone. The degree of cuticularisation or of lignification is probably of importance at least equal to that of the tubular thin walled structure.

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[15] Fr. Pat. 480637; *J.*, 1917, 131, and Ger. Pat. 297569, *J.*, 1917, 869.

[16] Ger. Pat. 297138; *J.*, 1917, 869.

[17] Eng. Pat. 17348, 1914; *J.*, 1917, 131.

[18] *Journ. Soc. Dyers and Col.*, 1916, **32**, 274; *J.*, 1917, 79.

Marine fibre is the subject of a report by D. C. Winterbottom to the South Australian Department of Chemistry.[19] This fibre, which is the resistant leaf sheath of *Posidonia australis*, is found beneath a bed of the living plant in the shallow waters of Spencer's Gulf. Both chemically and technically, it stands in a category by itself. It is harvested by dredgers, collected by means of powerful pumps, and subjected to a disintegrating and washing process either on the dredger or at special factories on shore. Three companies have been concerned in its development which, however, has not yet reached a commercial stage. The cleaned fibre is coarse and brittle, containing a large amount of mineral matter. It ranges from 2 to 8 inches in length but its textile possibilities are somewhat limited, though it might be mixed with jute or wool. It gives excellent results as an insulating material but its value for this purpose does not cover the cost of collection and purification. Chemically, the marine fibre is a highly pronounced lignocellulose, extremely resistant to chemical processes of hydrolysis. As the result of its occurrence in an aqueous medium, all the softer tissues of the plant subject to hydrolytic and bacterial influences have already been eliminated and the residual fibre is characterised by exceptional rot-resisting properties. For the same reason it does not yield readily to the ordinary paper-making processes and it is not considered a suitable raw material for that purpose, although it yields 63% of cellulose on chlorination.

Animal Fibres.

Wool. E. Seel and A. Sander[20] describe the modifications of the microscopic structure of the wool fibre under the action of alkalis, as shown after treatment with a 1% solution of caustic soda for 15 minutes at temperatures from 40° to 80° C. Different varieties of wool differ in their degree of resistance. The initial indications of attack take the form of longitudinal striations due to the wrinkling of the epithelial scales, so that the surface of the fibre assumes somewhat the appearance of a withered apple. The degree of action ranges from a simple swelling of the scales to the formation of pronounced furrows. At 70–80° C. the epidermal layer is disintegrated

[19] *S. Aust. Dept. Chem., Bull.* No. 4, 1917; *J.*, 1917, 542.

[20] *Z. angew. Chem.*, 1916, **29**, 261; *J.*, 1916, 886.

and the cuticle is ultimately completely detached from the fibre. Wool may be boiled with 1% sulphuric acid for an hour without structural modification, but if it has been previously affected by the action of alkalis it becomes extremely susceptible to attack by hot dilute acid and the striations thus produced are distinctly different from the wrinkling caused by alkali alone. The bearing of these observations on the operations of scouring, alkaline vat dyeing, and acid dyeing of wool is obvious and the use of strongly alkaline scouring baths may produce far reaching effects.

K. von Allworden[21] has also studied the modification of wool by alkalis. He claims to have separated from the alkaline extract a carbohydrate substance, yielding an osazone similar to galactosazone, to which he gives the name of *elasticum*. The deterioration of the wool by the action of alkalis is attributed to the removal of the elasticum. The presence or absence of elasticum may be detected microchemically by treating the fibre with half-saturated chlorine water. If the elasticum be present under normal conditions, characteristic globular excrescences are produced corresponding to the successive rows of scales, whereas in the case of damaged wool deficient in elasticum the swellings are either partially or wholly absent and in their place shreds of partially loosened scales are observed. Allworden believed his test to be definitely characteristic, depending on the presence or absence of the alkali-soluble elasticum, with which the physical resistance of the wool is supposed to be intimately and directly connected. K. Naumann,[22] however, has taken up the question and found that the elasticum reaction with chlorine water varies in degree with different types of wool and in different parts of the same fibre. The characteristic swellings are most regularly continuous in the middle portion of the fibre and diminish towards both ends. Certain samples of lambs' wool and coarse Australian cross-bred wool showed only a few irregularly distributed swellings. The reaction is much sharper if the wool be previously extracted with benzene. It is still too soon to pronounce a definite opinion on the diagnostic importance of the elasticum reaction or to admit its direct connection with the presence of a substance on which the elasticity of the fibre depends, but it is certain that no practical conclusions can be drawn from it unless the examination is extended over the entire length of the fibre.

O. Sauer[23] describes a method for detecting deterioration of wool by atmospheric influences, such as sunlight, consisting in determining the percentage of the total nitrogen which is soluble in a dilute alkaline solution of hydrogen peroxide. The optical refraction of wool and hair fibres has been determined by A. Herzog[24] for comparison with that of vegetable and artificial fibres, but the results have little diagnostic significance.

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[21] *Z. angew. Chem.*, 1916, **29**, 77; *J.*, 1916, 416.
[22] *Z. angew. Chem.*, 1917, **30**, 135; *J.*, 1917, 706.
[23] *Z. angew. Chem.*, 1916, **29**, 424; *J.*, 1917, 78.

E. V. Chambers[25] describes the recent progress made in the recovery of grease and potash from wool-scouring liquors. The enrichment in potash salts by repeated use of the cleansed scouring liquor, until it will repay the cost of evaporation and incineration, is best effected by treatment in a centrifugal separator in which the grease is skimmed off continuously from the layer nearest the centre. This is a very satisfactory process and should show a profitable return. Winterbottom[26] has published a report on the sources of potash in South Australia, in which a proposal is made for the recovery of lanolin by a simple process suitable to the somewhat primitive conditions under which wool-scouring is carried out in that colony, where sodium carbonate is employed without soap. It is pointed out that from the 3,500 tons of wool scoured annually in South Australia, 50 tons of lanolin might be recovered by simple hand skimming and refined by melting with wood-charcoal at a cost not exceeding £15 per ton.

Silk. In a paper published by L. Pigorini,[27] it is shown that the application of a dilute solution of ammoacetic acid to the leaves upon which silkworms were fed resulted in an increase in the weight and length of workable silk.

The weighting of silk may be regarded as a series of inorganic chemical reactions complicated and modified through being carried out in presence of a medium which is active in both a colloidal (electrical) and chemical sense. P. Heermann[28] discusses the various theories concerning the mechanism of this reaction and pronounces in favour of an electrical "ionetic" theory as the most rational explanation of the phenomena. The attraction of the silk for the dissociated stannic chloride depends on its electrical charge, and the amount of weighting increases with the degree of dissociation of the stannic chloride bath.

The tendering of weighted silk goods may be due to the development of acid or to oxidation, possibly under the influence of chlorine liberated from the absorbed basic stannic chloride. Splashes of sodium chloride are also exceptionally injurious, and the deterioration is strongly increased by exposure to light. Protective action against acids is obtained by treatment with salts of weak organic acids and against oxidation by the presence of substances more readily oxidisable than the silk fibroin. K. Homolka[29] recommends ammonium formate as both a neutralising and reducing agent; ammonium thiocyanate is recognized as having a markedly beneficial action; hydroxylamine salts are also protective. Schadd und Korteling[30] point out the beneficial protective influence of oxidisable organic substances containing nitrogen or sulphur, or both, and specifically recommend hippuric acid applied in the form of its sodium salt. Formaldehyde is also useful.[31]

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[24] *Chem.-Zeit.*, 1916, **40**, 528; *J.*, 1916, 832.

[25] *Journ. Soc. Dyers and Col.*, 1916, **32**, 61; *J.*, 1916, 417.

[26] *S. Aust. Dept. Chem.*, Bull. No. 2, 1916; *J.*, 1917, 289.

[27] *Arch. Farm. sperim.*, 1915, **20**, 225; *J.*, 1916, 806.

[28] *Mitt. K. Materialprüf*, 1915, **33**, 146; *J.*, 1916, 924.

For the recovery of tin salts from waste silk rags a solution of acid ammonium oxalate has been proposed;[32] the rags are steeped in the hot solution until the metallic compound is extracted; the metal salt is decomposed and precipitated by ammonia in excess, and when the filtered liquid is distilled, the excess of free ammonia and part of the combined ammonia are recovered, leaving a solution of acid ammonium oxalate in the residue ready for re-use.

Cellulose

The photochemical oxidation of cellulose, resulting in its ultimate discoloration and destruction under the atmospheric influence of light, air, and moisture alone, has been recognised from the earliest times and the controlled action of these influences, through the supposed intervention of ozone or hydrogen peroxide, has been the foundation of the ancient grass bleaching process. An investigation of this action has been carried out by C. Dorée and J. W. Dyer,[33] who have used a Cooper Hewitt mercury vapour lamp as the source of photochemical energy. Discoloration and ultimate disintegration were confined solely to the portions of the surface exposed to the light, and the properties of the product corresponded in all respects to those of oxycellulose produced by chemical oxidising agents.

The reaction between cotton cellulose and sodium hydroxide has been the subject of divergent views for many years, the balance of recent evidence being against the formation of definite soda-cellulose compounds, and in favour of the adsorption theory. A. Leighton[34] has reviewed and criticised previous work, showing that the earlier experimental methods have failed to allow for the adsorption of water as well as of sodium hydroxide from the solution. A method has been adopted whereby all the adherent solution is removed from the cellulose by centrifuging it at a high speed and the residual alkali determined gravimetrically. These results, combined with the data obtained from the alteration of the concentration of the removed solution, gave a series of values for the respective adsorption of water and sodium hydroxide which, plotted graphically, have the form of a smooth adsorption curve with no evidence of the formation of a chemical compound of the nature of alkali cellulose at any stage of concentration.

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[29] *Färber-Zeit.*, 1915, **26**, 17; *J.*, 1916, 417.

[30] Fr. Pat. 478007; *J.*, 1916, 1107.

[31] Fr. Pat. 477698; *J.*, 1916, 596.

[32] Beisenherz, Eng. Pat. 4901/1915; *J.*, 1916, 596.

[33] *J. Soc. Dyers and Col.*, 1917, **33**, 17; *J.*, 1917, 211.

The same author[35] has performed a similar series of experiments by the centrifugal method on the adsorption of aqueous acids by cellulose. Here, also, no chemical combination takes place at ordinary temperatures. Cellulose adsorbs sulphuric acid more than phosphoric acid and the latter more than hydrochloric acid. Selective adsorption is only pronounced at high concentrations of the acids and does not occur at all with phosphoric acid; it is stronger with hydrochloric than with sulphuric acid. When cotton is treated with small quantities of sulphuric acid, *e.g.*, 0·01–0·02%, and dried at a low temperature, its strength is not decreased but is even increased. Such acidified cellulose is more suitable for making cellulose derivatives, *e.g.*, viscose or cellulose acetate, than ordinary cellulose, giving solutions of good viscosity and improved solubility and threads of satisfactory strength.[36] It is stated that the favourable effect of such traces of sulphuric acid in the fibre is noted in the process of acetylation and a better effect is thus produced than when the acid is added to the acetylating mixture.

Fort and Pickles[37] have made a very careful investigation of the tendering of cotton yarn by solutions of acids and salts at various concentrations at 100° C. The results showed with remarkable regularity that the degree of tendering is proportional to the "strength" of the acids as indicated by their relative electrical conductivities or the velocity of inversion of cane sugar. In the case of salt solutions and mixtures of salts and acids, the laws of electrolytic dissociation were proved to govern the degree of tendering with few, if any, exceptions. This investigation is of the highest interest and suggestive importance, not only because of the conclusions established, but also on account of the problems which arise from it. What, for instance, is the difference in chemical terms between cellulose with high tensile strength and hydrocellulose with no strength at all? In the transition from one to the other the formation of soluble products is very small and the loss of strength is out of all proportion to the loss of weight, yet the infinite number of gradations between the two extremes, the result of hydrolytic action, can be measured by tensile strength tests almost as accurately as the inversion of cane sugar can be followed with the polarimeter. In the chemical groups affected resides the entire economic value of the cellulose, and a study of these relationships in their physical and chemical aspects would constitute an important piece of theoretical research.

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[34] *J. Phys. Chem.*, 1916, **20**, 32; *J.*, 1916, 249.

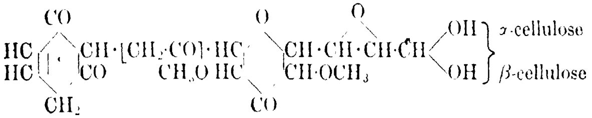
[35] *J. Phys. Chem.*, 1916, **20**, 188; *J.*, 1916, 464.

[36] Ger. Pat. 290,131, *J.*, 1916, 533, and *Kunststoffe*, 1916, **6**, 17; *J.*, 1916, 538.

[37] *J. Soc. Dyers and Col.*, 1915, **31**, 255; *J.*, 1916, 38.

Condensation products of cellulose with formaldehyde have long been known and have proved of great service in the artificial silk industry. The formation of these products takes place as the result of a somewhat complex and obscure series of reactions of mild dehydration. According to a recent patent[38] the formaldehyde must first be converted into trioxymethylene. Cellulose is treated with formaldehyde in presence of ferric chloride or organic acids, with or without dehydrating agents such as alum or calcium chloride; it is then dried under high vacuum and trioxymethylene is thus produced; on stoving, the condensation product is formed. This interesting product was first discovered by Eschalier[39]; when hydrolysed by mineral acids the formaldehyde is again liberated. The treatment makes the cellulose more resistant to water and improves the "wet strength" of artificial silk.

Cross and Bevan[40] have contributed further notes on the reactions of the lignone complex in lignocelluloses. They have studied the quantitative reaction with phloroglucinol and find that a considerable time is required to obtain maximum combination. Combination also takes place between lignocellulose and pyrogallol. The formation of volatile acids by hydrolysis of the complex may be appreciably increased by oxidation. The ultimate products of hydrolytic oxidation are acetic, oxalic, and carbonic acids. The authors propose a structural formula for the lignone complex, thus:—



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[38] La Soie Artificielle, Fr. Pat. 477655; J., 1916, 597.

[39] Fr. Pat. 374724; J., 1908, 821.

[40] *J. Soc. Dyers and Col.*, 1916, **32**, 135; *J.*, 1916, 628.

which is in accordance with the main characteristic reactions, such as the chlorination reaction, the formation of sulphonates with bisulphites, the maximum production of acetic acid by hydrolysis and oxidation. The quantitative results obtained by chromic acid oxidation in presence of dilute hydrolysing acid suggest that a portion of the complex escapes resolution, and the hypothesis is put forward that this component has a pyrone configuration and contains the methoxyl residues. This hypothesis is supported by the observed production of maltol by incipient roasting. The theoretical speculations which form the substance of the latter part of this paper are extremely suggestive, but require very considerable elucidation and co-ordination before they can be formulated in any decisive manner.

Cellulose Esters.

The manufacture of cellulose esters and plastics has been stimulated by war conditions, but the processes which are undergoing development are mainly of pre-war origin, and there are few additions of primary importance to the published literature.

Nitrocellulose.—Though falling outside the period covered by this review, attention must be paid to an investigation by C. G. Schwalbe and A. Schrimpff[41] on the comparative nitration of cotton and wood celluloses. This is of interest as showing the trend of German research in the domain of cellulose explosives and plastics during the early stages of the war before the scarcity of cotton had become acute. The investigations showed that wood cellulose was capable of nitration, both for gun-cotton and celluloid, to give products satisfying all the specifications established for nitrated cotton, provided it were previously transformed into thin tissue paper of suitably open texture. The form of wood cellulose employed by Schwalbe was soda wood pulp, which is free from the objectionable resinous impurities present in sulphite wood pulp, but there is reason to believe that later practice in Germany has adopted the more normal sulphite wood pulp after submitting it to a special de-resinifying treatment by extraction with dilute alkali.

Nishida[42] has investigated under comparative conditions the relative suitability of various forms of cotton cellulose, wood, bamboo, and straw celluloses as raw materials for the manufacture of celluloid. Materials other than loose cotton and cotton yarn are best employed in the form of tissue paper. With an acid of given composition it is necessary to keep the product of the temperature and the time of nitration at a constant value, varying with different materials according to the ease of nitration; when using paper thicker than tissue paper a correction must be made according to thickness.

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[41] *Z. angew. Chem.*, 1914, **27**, 662; *J.*, 1915, 152.

[42] *J. Ind. Eng. Chem.*, 1916, **8**, 1096; *J.*, 1917, 27.

Cellulose acetate. J. Boeseken[43] and others have published an article on the mechanism of the acetylation of cellulose and starch. The primary function of the catalyst is to act as a common solvent of the carbohydrate and the acetic anhydride and the rate of acetylation is limited by the rate of diffusion of the acetylating mixture in the carbohydrate, which is much slower than the actual acetylation. Hence the relative surface of colloidal carbohydrates is probably approximately measured by the velocity of acetylation.

In connection with the manufacture of cellulose acetates several new patents may be noted. For instance, it has been proposed to introduce small proportions of nitrated groups into the cellulose during the stages preliminary to acetylation.[44] A form of cellulose acetate soluble in tetrachloroethane, giving an unusually viscous solution, is obtained when using sulphuryl chloride as the acetylating catalyst.[45] In one of the later patents of the Dreyfus series, in which sulphuric acid is the catalyst employed,[46] provision is made for conducting the major part of the reaction below ordinary atmospheric temperature, only allowing it to rise to about 25°C. towards the end. In another,[47] it is stated that, whereas sodium bisulphate is in itself not an active acetylation catalyst, when used in conjunction with a little free sulphuric acid it shows a technical advantage. Acetylation in presence of trioxymethylene with a sulphuric acid catalyst is claimed by the Soc. Prod. Chim. des Usines du Rhône.[48] A form of cellulose acetate which retains the original structure of the fibre is made by treating cellulose in a preliminary bath consisting of a strong solution of zinc chloride in acetic acid containing a little water, and then acetylising with acetic anhydride in presence of benzene.[49]

Attempts have been made to prepare the lower acetates of cellulose without the use of acetic anhydride. Products containing up to 30% of combined acetic acid have been obtained by a process in which large proportions of sulphuric acid are employed with acetic acid.[50] These products, though soluble in certain special solvents, have probably little technical value, being derivatives of very profoundly modified cellulose.

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[43] *Rec. Trav. Chim. Pays-Bas*, 1916, **35**, 320; *J.*, 1916, 164.

[44] Eng. Pat. 8046/1915; *J.*, 1916, 39.

[45] Eng. Pat. 21016/1915; *J.*, 1916, 39.

[46] Fr. Pat. 478023; *J.*, 1916, 1152.

[47] Fr. Pat. 475160; *J.*, 1916, 19.

[48] Eng. Pat. 7773/1915; *J.*, 1916, 392.

[49] U.S. Pats. 1236578 and 1236579; *J.*, 1917, 1092.

[50] Eng. Pat. 75/1915; *J.*, 1916, 39.

Solvents and Plastics.

The search through the by-ways of organic chemistry for plastifying agents (so-called camphor substitutes) for cellulose esters still continues on somewhat empirical lines, preference being given to liquids of high boiling point sparingly soluble in water. H. Dreyfus[51] specifies the principles to be observed in compounding mixtures of solvents, non-solvent diluents, and plastifying agents, the proportions being varied according to the rate of volatilisation and solvent powers. A long list of organic compounds and types capable of acting either as solvents or plastifying agents with cellulose acetates is given. Triarylphosphates are used to reduce inflammability and liquids of very high boiling point, such as carefully purified benzyl alcohol and various esters of glycerol, are used to impart flexibility. If aromatic halogen compounds are employed, the halogen should be in the nucleus, not in the side chain.

As special solvents for cellulose acetate the alkyl or alkylidene ethers of glycerol chlorohydrins, particularly methylene chlorohydrin, have been proposed.[52] A combination of cellulose acetate with a fluent reaction product of formaldehyde and phenol is the subject of another specification.

W. G. Lindsay has been particularly prolific in patented suggestions for solvents and softening agents for cellulose acetate plastics. Solvent mixtures include combinations of acetone, methyl acetate, methyl alcohol, trichloroethylene, epichlorohydrin, and chloroform. As a non-volatile softening agent an arylsulphonamide, particularly *p*-ethyltoluenesulphonamide, is specified, being employed in the proportion of 30–40% of the cellulose acetate, in conjunction with triphenylphosphate and volatile solvents. Gelatinisation of cellulose acetate is induced at the ordinary temperature by a mixture of benzene and methyl alcohol containing a little water,[55] softening agents are added and the mass is kneaded, heated, and pressed. Tetrachloroethylacetanilide in presence of ethyl alcohol dissolves cellulose acetate while hot, but not in the cold.[56]

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[51] Additions to Fr. Pat. 432264; *J.*, 1916, 10.
[52] Ger. Pat. 288267; *J.*, 1916, 356.
[53] U.S. Pat. 1173337; *J.*, 1916, 465.
[54] U.S. Pats. 1188797 to 1188800; *J.*, 1916, 887; 1203098; *J.*, 1916, 1256; 1226339 to 1226343; *J.*, 1917, 707; 1229485 to 1229487; *J.*, 1917, 869.
[55] U.S. Pat. 1199395; *J.*, 1916, 1215.
[56] U.S. Pat. 1218954; *J.*, 1917, 450.

Dihydroxydiphenyldimethylmethane is specified by Beatty[57] and phenyl salicylate by Mork and Esselen[58] as suitable components of plastic compositions.

Nitrocellulose Plastics.—The use of phenyl benzoate or its homologues is claimed in making plastic masses of pyroxylin base.[59] In making plastic masses with nitrocellulose, Lindsay[60] kneads moist pyroxylin with liquid tricresylphosphate which is insoluble in water and from the resulting mass the water may be expelled by pressing. According to Masland[61] pyroxylin is combined with from 2 to 40 % of aldol and 10 to 60 % of a vegetable oil, such as castor oil, the total amount of aldol and oil being 10–75 % of the mixture.

Viscose. A plastic mass may be prepared from peat, a portion of which has been gelatinised by the viscose process to make a binding material for the remainder.[62]

ARTIFICIAL TEXTILES.

Artificial Silk. L. P. Wilson[63] at the Annual Meeting of the Society gave a sketch of the origins and development of the artificial silk industry. The relative and successive importance of the nitrate, cuprammonium, and viscose processes is shown and the methods employed are briefly indicated. This *résumé*, although containing no new information, is of considerable interest because all the essential factors are set out in their true perspective. The progressive increase both in dry and wet strength of viscose silk in recent years is worthy of notice. The tensile strength has been raised from 1·1 grm. per denier, dry, and 0·35, wet, in 1907, to 1·4, dry, and 0·55, wet, in 1913, and latterly to 1·75, dry, and 0·75, wet, in 1917. A series of photomicrographs shows the variations of the contour of the cross-sections of artificial silks with differences in principle or detail of the mechanical conditions of spinning. S. J. Pentecost[64] has contributed a note on the tensile strength of artificial silk used in the lace and hosiery industries and has confirmed the fact that the viscose product is superior to all the others both in the dry and wet state, whereas many specimens of the nitrate silk are practically worthless.

The relative and absolute concentrations of the sulphuric acid and sodium sulphate in the coagulating bath used in the viscose process are matters of some importance from the point of view of speed of production and quality of thread and have been the subject of patents. The Vereinigte Glanzstoff Fabriken[65] specify a bath containing 160 grms. of real sulphuric acid and more than 240 grms. (*e.g.* 320 grms.) of sodium sulphate per litre, suitable for use at 45°–50° C. Another patent by Verhave[66] specifies a solution containing 7–11% of sulphuric acid and two or more soluble sulphates, in such quantity that the liquid contains at least 5 grm.-mols. of SO_4'' ions to 3 grm.-mols. of H' ions; magnesium sulphate is employed in conjunction with sodium sulphate.

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[57] U.S. Pat. 1188356; *J.*, 1916, 923.

[58] U.S. Pat. 1193198; *J.*, 1916, 961.

[59] U.S. Pat. 1161063; *J.*, 1916, 40.

[60] U.S. Pat. 1233374; *J.*, 1917, 1004.

[61] U.S. Pat. 1234921; *J.*, 1917, 1044.

[62] U.S. Pat. 1213115; *J.*, 1917, 334.

[63] *J.*, 1917, 817.

[64] *J.*, 1916, 586.

A solution of nitrocellulose which is stated to be particularly suitable for spinning in air, as the threads solidify almost immediately, is prepared by adding to nitrocellulose solution anhydrous aluminium chloride, sodium formate, aluminium phosphate, and aluminium nitrate and thinning with water, alcohol, or ether to the desired consistence.[67]

Paper yarn textiles.—The shortage of textile fibres in Germany has greatly stimulated the manufacture and use of paper yarn textiles, which are made in two principal grades, *viz.*, as a substitute for jute, for sacking and cable insulation purposes, and as a substitute for cotton or wool for wearing apparel and general domestic uses. For the latter purpose the manufacture of the finer grades of paper cloths has attained such perfection that this material is to be regarded as something more than a substitute and has established itself in the public taste on its own merits as a permanent institution.[68] Besides the variations obtained by using different qualities of paper, a large variety of effects is produced by after-treatment of the yarns with chemical preparations which increase the strength and resistance to moisture. One of the most suitable treatments for sacking consists in sizing in a bath containing glue, tannin, and sodium silicate,[69] afterwards fixing in a solution of aluminium formate. This produces an increase of 10% in the dry tensile strength and 30% in wet strength. Tannin and gelatin together give a hard, stringy feel, but tannin used alone increases the strength in the dry state and gives a soft pliable thread, while tannin fixed by basic aluminium acetate favours elasticity. Soap fixed by aluminium acetate acts as a softener and to a certain extent reduces the absorption of water but does not increase the strength.

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[65] Ger. Pat. 287955; *J.*, 1916, 174.

[66] Eng. Pat. 2485/1915; *J.*, 1916, 250.

[67] Fr. Pat. 478461; *J.*, 1916, 1152.

[68] Massol, *Z. angew. Chem.*, 1917, **30**, 97; *J.*, 1917, 543.

[69] A. Kertesz, *Chem.-Zeit.*, 1917, **41**, 43; *J.*, 1917, 287; also L. Cassella und Co., *Chem.-Zeit.*, 1917, 41, Rep. 56; *J.*, 1917, 592.

PAPER MANUFACTURE.

General.

Certain reports on the development of the paper-making industry in various parts of the world are worthy of notice. W. A Hargreaves,[70] reporting to the South Australian Government on the prospects of the establishment of the industry in that colony, comes to the conclusion that the only immediately available practicable raw material is cereal straw, of which over 500,000 tons is available annually within a radius of 100 miles from the principal seaport, at which the straw could be delivered at a price not exceeding 30s. per ton. Port Adelaide is favourably situated for the operation of a mill making 5000–6000 tons of fine printings and writings per annum, also for the establishment of a straw-board mill. In a report to the U.S Government,[71] statistics are given of the production and imports of wood pulp in Russia. Considering the vast resources of the country, the figures in both cases are relatively small but show that there is a steady development of the wood pulp industry, while the production is many times larger than the imports, which come principally from Finland and Germany.

The wood pulp and newsprint industry of Canada is dealt with in a very interesting and important paper by O. F. Bryant.[72] This article contains a description of the modern methods of manufacture of wood pulp and newsprint paper and is well worth perusal in the original by anyone interested in the practice of this industry. The total production of pulp in Canada was 1,074,805 tons in 1915, of which 743,796 tons was mechanical pulp

Fibres.

The search for new fibres in view of a possible shortage in the world's supplies of pulp wood continues vigorously. The war has stimulated this search in two ways: 1. The enormous destruction and abnormal consumption of constructional materials during the war must have its effect on the supply of wood available for pulping purposes for many years afterwards. 2. The consolidation and development of the British Empire as the result of the war is producing a movement which must favour the demand for pulp produced within the Empire rather than in neutral countries in the German zone.

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[70] *S. Aust. Dept. Chem*, Bull. No. 1, 1916, *J.*, 1917, 27.

[71] *U.S. Comm. Rept.*, No. 277, 1915; *J.*, 1916, 108.

[72] *Pulp and Paper Mag. of Canada*; *J. Roy. Soc. Arts*, 1917, **65**, 619, 631, *J* 1917, 1043; also *Board of Trade J.*, Feb. 17, 1916; *J.*, 1916, 302.

The manufacture of common wrapping paper from sugar cane bagasse is being carried on at Preston, Cuba, the output being consumed locally.[73] Bagasse, however, is not a material which is likely to find any really extensive application in the manufacture of white papers.

Zacaton (Mexican whisk) is a Central American grass of which the roots are exploited for brush manufacture. The grass requires somewhat severe conditions of digestion and yields 16-50% of a first-class fibre. The supply is somewhat restricted but sufficiently concentrated to constitute a small practicable source of pulp material.[74]

The Imperial Institute[75] has received and examined samples of Tambookie grass and papyrus from South Africa. Both these are practicable raw materials for the manufacture of excellent paper pulp in the country of origin, but owing to the relatively low yields of cellulose and other economic reasons the transport of these raw materials to this country would be unprofitable.

The question of the utilisation of cotton stalks has been discussed by W. B. Nanson.[76] Cotton stalks are available in America to the amount of 52 million tons annually, and Nanson proposes to make an overhead digestion of the chopped stalks with caustic soda under high steam pressure. This proposition has been put forward from time to time for many years but it is not technically a very attractive one. The cotton stalk contains, besides the valuable bast fibres, a preponderating proportion of very short wood fibres as well as a considerable contamination of dark coloured bark residues, and it is doubtful whether the cost of treatment would be covered by the value of the product obtained.

Some new fibre materials of interest have been tested at the Imperial Institute.[77] *Ecdeiocolea monostachya* is a rush-like plant found only in West Australia. It behaves very similarly to esparto grass but the pulp is liable to be contaminated by specks of wax or resin which can only be eliminated by increasing the severity of the treatment. *Neoboutonia macrocalyx* is a tree growing in the East African Protectorate; the wood is very suitable for the manufacture of soda pulp. G. E. Walsh[78] has contributed an article on the waste products of crop plants cultivated in the United States which might serve as a basis for pulp material. The material available in largest quantity is the residue of the maize crop; corn stalks may be separated by stripping the outer part for paper-making, leaving the less fibrous inner portion for cattle fodder. Broom corn is superior to ordinary Indian corn as a pulp material but the quantity available is not so large. Some notes by R. S. Pearson[79] on the development of Indian forest products show that renewed interest is being turned to the manufacture of paper pulp from materials growing in the country and that some of the jungle grasses which cover large tracts of territory are destined to play a prominent part in the paper industry not only of India but of the world. Incidentally it is noted that the output of the Indian paper mills before the war was about 25,000 tons and the imports in 1914–15 were 51,300 tons.

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[73] *J. Roy. Soc. Arts*, 1915, **64**, 132; *J.*, 1916, 39.

[74] Brand and Merril, *U.S. Dept. Agric.*, Bull. No. 309, 1915; *J.*, 1916, 417.

[75] *Bull. Imp. Inst.*, 1916, **14**, 163; *J.*, 1916, 1008.

[76] *Paper Making*, 1916, **35**, 371; *J.*, 1917, 131.

[77] *Bull. Imp. Inst.*, 1917, **15**, 1; *J.*, 1917, 1004.

[78] *Paper Making*, 1917, **36**, 283; *J.*, 1917, 1091.

Wood and Wood Pulp

Whatever may be effected in the utilisation of other fibres and vegetable wastes, wood must always remain the principal foundation of the paper industry. Development is to be looked for in the systematic exploitation of untapped sources and especially in the utilisation of inferior species and by-products of the timber industry which have hitherto been regarded as commercially unsuitable.

An outline of the sulphite wood pulp process is given in a useful paper by A. Smith,[80] which may be studied in conjunction with the article by Bryant already mentioned.[72]

The closest attention deserves to be paid to a publication by A. W. Schorger[81] on "The Chemistry of Wood." This is the most important article on analytical methods which has appeared for a long time and takes rank as a classical standard for laboratory work in this domain. The author recognises the fundamental factors which govern the results obtained, particularly the importance of the mechanical preparation of the sample and the fact that no extraction treatment with hydrolytic agents is specific or final, but that digestion, even with water and still more with dilute alkali, is a chemical and not merely a solvent process. The details of the different determinations are too lengthy for quotation and must be obtained from the original article; it is obvious that with reactions of this character consistent results can only be achieved by rigid adherence to the conditions prescribed. The definition of "cellulose" as the residue left after alternate treatments with chlorine gas and sodium sulphite until the disappearance of the colour reaction is perfectly legitimate and disposes of the impression that cellulose of whatever origin is necessarily one and the same definite chemical entity with "impurities." This residue is a complex of associated groups varying with the origin but capable of classification according to chemical types, which in the case of wood cellulose correspond with the natural differentiation between conifers and broadleaf trees. The question of the propriety of boiling out the raw material with dilute caustic alkali before chlorination is not definitely settled. Such treatment apparently reduces the yield of cellulose by 1–3%, but on the other hand its omission may very possibly leave in the residue pectic substances which certainly do not belong to the cellulose complex, more or less, according to the character of the raw material.

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[79] *J.*, 1917, 631.

[80] *J.*, 1916, 282.

[81] *J. Ind. Eng. Chem.*, 1917, **9**, 556; *J.*, 1917, 867.

A study of the chemical modifications taking place in decayed wood has been made by R. E. Rose and M. W. Lisse[82] who have analysed samples of Douglas fir at progressive stages of decay. The great increase in products soluble in caustic alkali takes place chiefly at the expense of the cellulose; there is also a progressive disappearance of the groups yielding acetic acid and furfural, while the methylfurfural and methoxyl groups are resistant.

The utilisation of the vast quantities of wood waste produced in the United States is the subject of a paper by A. D. Little.[83] The waste from the long leaf yellow pine industry alone is sufficient to produce 40,000 tons of "kraft" paper daily by the sulphate process, besides 3000 tons of rosin and 600,000 gallons of oil of turpentine by suitable extraction processes. Particulars of a process for extraction of resinous wood wastes by petroleum spirit are given by Palmer and Boehmer.[84] The stump wood is most highly resinous and therefore most suitable for the recovery of turpentine, resin, and oils either by volatile solvents or destructive distillation. Extraction of these products by dilute alkalis does not appear yet to have given satisfactory results.

From sawdust or similar small waste, alcohol is produced by the Ewen-Tomlinson process, the yield being 10 gallons of 95% alcohol per cord of sawdust or hogged wood waste containing 50% of water. Processes patented by Nicolardot and by Gazagne and Demuth relate to the details of the saccharification of sawdust for the production of alcohol.[85] One of the major obstacles is the difficulty of obtaining anything approaching complete saccharification of the cellulose. This difficulty is said to be surmounted by using only sufficient moisture to damp the material and supplying sufficient hydrochloric acid gas, preferably under pressure, to produce with the moisture present an acid of at least 10 % concentration. With 10 % hydrochloric acid cellulose is completely hydrolysed to dextrose[86].

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[82] *J. Ind. Eng. Chem.*, 1917, **9**, 284; *J.*, 1917, 457.

[83] *Met. and Chem. Eng.*, 1916, **14**, 133; *J.*, 1916, 301.

[84] *J. Ind. Eng. Chem.*, 1916, **8**, 965; *J.*, 1916, 975.

[85] Fr. Pats. 476,696 and 476,077; *J.*, 1916, 613.

Wood pulp waste liquors.—The manufacture of alcohol from waste sulphite liquors, without restrictions, for use as motor spirit, has been recommended in Sweden provided the sulphite alcohol is denatured with benzol.[87] A process for the preparation of easily fermentable liquor is described by Tartar,[88] consisting in recovering the sulphur dioxide as far as possible by concentration in presence of sulphuric acid and oxidising the residual traces with permanganate; a specially acclimatised yeast is then not required. Oman[89] points out that it is practically impossible to neutralise sulphite liquor with chalk alone and recommends the careful neutralisation of the lye in the first place with chalk and subsequently to an ascertained optimum limit (0·02–0·03-N acidity) by the addition of the calculated amount of milk of lime. A general account of the main proposals for the utilisation of waste sulphite lyes is given in a paper by Beveridge.[90] Among the various patents for the utilisation of these lyes recently published, a proposal by M. Muller[91] may be noted for reducing the sulphuric acid of nitre cake by roasting it with the waste lyes and recovering the sulphur dioxide produced. No propositions of really outstanding importance have been put forward for the effective utilisation of the liquors on the large scale in the recent patent literature, but many small applications, *e.g.*, for binding agents for various purposes, have been suggested.

In connection with soda pulp waste lyes a certain amount of industrial research has been done on the lines of destructive distillation with recovery of methyl alcohol, acetone, light, and heavy oils. Following a patent taken by A. H. White,[92] a further description of the process is given in a paper by the same author.[93] This process is of considerable importance owing to the novel arrangement of the retort, whereby the process is carried out in a semi-continuous manner. The liquor is caused to flow down inclined heated tubes in which the vapours are allowed to remain for from 5 to 150 seconds. An aqueous distillate amounting to 65·5 % of the black liquor treated is obtained, containing 3·81 % of methyl alcohol and 0·56 % of acetone by vol. The voluminous carbonaceous ash acts in some degree as a catalyst, facilitating the splitting up of the volatile matters; the tar contains 50% of phenolic constituents. The best results are produced at 288°–316°C. This process has so far only been worked in an experimental plant, but from the results published there is every reason to expect that it will form the starting-point of an industrial recovery of valuable by-products, the principle of which will ultimately become standard practice in all mills working the soda process.

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[86] Eng. Pat. 107,219/1916; *J.*, 1917, 973.

[87] *Board of Trade J.*, Jan. 27, 1916; *J.* 1916, 192.

[88] *J. Ind. Eng. Chem.*, 1916, **8**, 226; *J.*, 1916, 483.

[89] *Papierfab.*, 1915, **13**, 534, 553; *J.*, 1916, 172.

[90] *J.*, 1916, 563.

[91] Ger. Pat. 297,374; *J.*, 1917, 870.

[92] U.S. Pat. 1,197,983; *J.*, 1916, 1106.

[93] *Met. and Chem. Eng.*, 1917, **16**, 182; *J.*, 1917, 383.

In connection with the same subject, J. C. Lawrence[94] describes a process for the destructive distillation of esparto black lyes. The experiments here recorded are the outcome of researches communicated by Rinman, who was the originator of the process. The concentrated black liquor is mixed with a calculated proportion of lime and the dried mixture is distilled on trays in presence of superheated steam. Owing to the excess of lime and the considerable percentage of sodium acetate in the liquors, acetone and not methyl alcohol is the main constituent of the aqueous distillate and the process is designed in the main for the production of acetone. The only products include a solid constituent corresponding to a portion of the esparto wax removed by the digestion liquors, which can be separated in a utilisable form by fractional condensation. Comparing the two processes, White's and Rinman's, the prospects of economic success are apparently in favour of the former process on account of the complication and expense involved by the introduction of lime in the latter and the greater difficulty of lixiviating the soda from the ash. Special points, however, may determine the ultimate result in a different way, as for instance, the feasibility of mechanical realisation, cost and life of plant, value of the respective products, etc., and much pioneer work remains to be done before either can be placed on a commercial footing as an adjunct to a wood or esparto pulp mill.

The black lyes from esparto boiling contain, besides a small proportion of wax and about 5% of acetic acid in the form of sodium acetate, a substantial amount of a pentosan (xylan) and, as the main constituent, the sodium salt of an acid derivative of the lignin, having many points of resemblance to Lange's "lignic acid." C. Budde[95] has studied the possible utilisation of these substances and has proposed a process whereby the concentrated liquor is mixed with a definite quantity of sulphuric acid or nitre cake. The earlier portion of the distillate contains acetic acid and furfural and the latter portion, after destructive distillation has set in, becomes alkaline, yielding tarry oils and ammonia. The soda may be recovered as sodium sulphide and may be worked up in the form of a causticised liquor. By varying the conditions and avoiding destructive distillation the acetic acid, 5%, and the furfural, 1·5 , may be recovered as before and the lignic acid residue in the still, "esparto resin," collected in the form of a black sintered mass. It has certain applications as a varnish or shellac substitute, and yellow to brown colouring matters may be prepared from it

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[94] *Met. and Chem. Eng.*, 1917, **16**, 416; *J.*, 1917, 543.

[95] *J.*, 1918, 401.

Special Digestion Processes

Among the many patents which have been published in connection with the manufacture of cellulose pulp from fibrous raw materials it is only possible here to mention a few which attract special attention on account of some novel interest. One of these relates to a process devised by Jardine and Nelson[96] principally for the manufacture of pulp by the bisulphite process from bamboo and similar materials which are mixtures of lignocellulose with substantial quantities of pectocellulose. While the "free" sulphurous acid is a specific reagent towards the lignin, it is ineffective with regard to the pectin, for the removal of which a basic digestion liquor is required. The combined reaction is obtained by using a base yielding a soluble neutral sulphite, such as a liquor obtained by the action of sulphur dioxide on a suspension of magnesium oxide in water. The higher the temperature at which this liquor is prepared the higher is the proportion of base to "free" acid dissolved. From a liquor prepared at 13 C. or higher and containing 0·8 of "free" SO_2 the whole of the free acid is absorbed in the reaction with the lignin, leaving a basic liquor which hydrolyses the pectin. A process for the fractional digestion of material under alternate acid and basic conditions is described by C. Harnist,[97] in which a solution of ammonia is used in conjunction with sulphur dioxide so that the material is gradually digested with predominance of one or the other alternately. The use of ammonia is likely to prove too costly on a manufacturing scale, but the process lends itself readily to the recovery of the reagents and to the preparation of by-products utilisable as fodder or fertiliser. The principle of fractional digestion has been very successfully applied to the soda process by W. Raitt.[98] The readily soluble pectic and gummy matters are extracted at a moderate temperature with a partially exhausted caustic liquor and the more resistant lignin is then attacked by a fresh strong caustic liquor by digestion at a high temperature. The removal of the gummy matters before a high digestion temperature is reached has a remarkable effect on the colour of the finished cellulose, and unbleached soda pulps produced in this way are almost as bright in colour as sulphite pulps. S. D. Wells[99] suggests that sufficient sodium hydroxide is adsorbed by wood chips from a 6 solution to perform the major part of the reaction at that concentration, and that copious dilution of the liquor by the condensed steam after the first stage is advantageous, as it facilitates the migration of the excess of sodium hydroxide from the digested cellulose and so moderates its destructive action in the later stages. A novel system of digestion is described by M. A. Adam[100] in which the finely ground material, *e.g.*, mechanical wood pulp of long fibre, together with an acid digestion liquor, is passed continuously through a digester at such a rate that it is exposed to a temperature of 150° C. for 30–40 mins. This process is only applicable to previously ground material in which the time consumed in penetration is reduced to a minimum; it can also be applied to the hydrolysis of sawdust for the production of fermentable sugar.

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[96] Eng. Pat. 2509/1915, *J.*, 1916, 533.

[97] Fr. Pat. 477,895, *J.*, 1917, 132.

[98] Eng. Pat. 16,488/1915; *J.*, 1916, 1009.

Bleaching.

In pulp-producing countries the production of bleach liquor from chlorine made by electrolysis, with caustic soda as a by-product, is becoming standard practice. This is particularly the case with the large American wood pulp paper mills. Some notes are published by J. Yamasaki[101] on the working of the Billiter-Leykam electrolytic cell, which is one of the most successful systems in Germany and Austria. The caustic liquor produced had a concentration of 3·5–4·5-*N* and the gas contained 95 of chlorine. With carbon anode and current density of 6–7 amps. per sq. dcm., the E.M.F. was 3·6 volts at 60° C. and 4·2 volts at 45° C.; the current efficiency was 92 . T. H. Nash[101A] has designed an interesting plant for the continuous bleaching of paper pulp by mixing it with bleach liquor and passing it through a series of intercommunicating containers fitted with paddles which transport the stuff gradually and uniformly from one end to the other.

Sizing.

In the sizing of paper the mechanical emulsifying process enables many unsaponifiable substances to be used in combination with the ordinary resin size, which otherwise could not be uniformly incorporated therewith. Whether the majority of these foreign substances have much real sizing efficiency may still be somewhat doubtful, particularly if their melting or sintering properties differ materially from those of common rosin. An emulsifying apparatus is described by Kniffler and Oppen[102] in which heated size is forced under high pressure beneath the surface of water and the pressure and temperature are suddenly lowered. De Cew specifies the emulsification of 15 % of paraffin wax with the resin size[103], this is stated to produce a kind of substitute for waxed paper. The admixture of 1 % of a rubber product with resin size is also claimed.[104]

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[99] *J. Ind. Eng. Chem.*, 1916, **8**, 601; *J.*, 1916, 887.
[100] Eng. Pat. 17,846/1915; *J.*, 1917, 544.
[101] *J. Chem. Ind., Tokyo*, 1916, **19**, 257; *J.*, 1916, 598.
[101A] Eng. Pat. 100,993/1916; *J.*, 1916, 923.

Coumarone and indene, constituents of certain fractions of coal-tar distillates, are resinified by treatment with sulphuric acid; 5–10 parts of such artificial resins are melted with 1 part of ordinary rosin and the mixture is saponified to an emulsion suitable for sizing paper.[105] De Cew[106] prepares an ammonium resinate size in presence of an excess of free ammonia by forcing a cold thick size into an ammoniacal solution. Gemmell and Milne[107] have also patented a size made with ammonia or borax which is intended to be decomposed with alum before being added to the stuff in the beater. The combination of a colloidal emulsion of gelatin, alum, and resin size for use in tub-sizing is specified by Sindall and Bacon.[108] A novel idea in connection with surface-sizing of paper is put forward by R. Clavel,[109] who produces by artificial means a layer of froth in the sizing and the fixing baths and passes the paper through the foam instead of through the liquid. The most economical and effective way of utilising starch in the manufacture of paper is to apply it to the surface of the web at some point in its passage over the machine. H. M. Wheelwright[110] has devised a very satisfactory arrangement for applying a solution of starch or "feculose" to the surface of the moist paper at the press-rolls. This arrangement, which is simple and does not interfere with the rate of output of the paper, is likely to prove of considerable importance and utility in giving starch-finishes to printing and writing papers with most efficient results, and it deserves the close attention of papermakers.

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[102] U.S. Pat. 1,215,034, *J.*, 1917, 334.

[103] U.S. Pat. 1,171,697, *J.*, 1916, 533. Eng. Pat. 13,588/1915; *J.*, 1916, 597

[104] U.S. Pat. 1,204,056, *J.*, 1916, 1257.

[105] Eng. Pat. 17,576/1915, *J.*, 1916, 1215. U.S. Pat. 1,194,866; *J.*, 1916, 1009.

[106] U.S. Pat. 1,223,158; *J.*, 1917, 593.

[107] Eng. Pat. 104,012/1916, *J.*, 1917, 383.

[108] Eng. Pat. 10,320/1915, *J.*, 1916, 887.

[109] Eng. Pat. 101,855/1915; *J.*, 1916, 1215.

[110] U.S. Pat. 1,195,888, *J.*, 1916, 1009.

Beating.

A really useful piece of technical research has been carried by A. E. Sunderland,[111] who has determined the effect of adding the colour, size, and alum to the stuff in the beaters in six different orders. The addition of these ingredients should not be made indiscriminately, as the order of the additions has a marked influence on the economical fixation of the colouring matter. The best results are obtained by adding to the pulp first the dyestuff solution, next the alum, and lastly the size, the quantity of alum being less for basic dyestuffs than with acid colours. Too much alum in the former case will even strip some of the colouring matter off the fibre.

The question of the numerical determination of the degree of beating has always been awaiting a simple and accurate solution. A perfectly satisfactory method has not yet been found, even for comparative determinations. A proposal has been made[112] to measure the viscosity of the pulp moving round the beater trough by suspending resistance rods in the path of flow and allowing the rods to rotate the suspension shaft against the spring of a dynamometer. This method is so much influenced by secondary factors that it is not likely to prove acceptable in practice. Another method, which is open to less objection, is based on the measurement of the rate of draining of the water from the pulp through a wire cloth. Useful indications are obtained on this principle from an apparatus designed by M. Riegler and put on the market by L. Schopper of Leipzig.[113]

Paper Machines.

A form of strainer differing completely from all previous types has been introduced by the Watford Engineering Works, Ltd.,[114] the straining surface being an inclined plane formed by horizontal rollers revolving at increasing speeds as the pulp flows down the incline. The narrow spaces between the rolls constitute the straining slits and the knots which fail to pass through are thrown off by the last roller into a receptacle. An apparatus for automatically regulating the dilution of the pulp and its flow on to the machine has been patented by Trimbey[115]; its operation is based on the frictional resistance of the pulp. T. D. Nuttall[116] has proposed what appears to be a very advantageous self-contained scheme for distributing power and steam to the beaters and paper machine, according to which each group is treated as a complete unit with its separate steam engine from which power is transmitted directly to the beaters and in the form of electricity to the paper machine units, while the exhaust steam discharges into a common main from which the drying cylinders are fed. An auxiliary air-blast arrangement for accelerating the drying on the cylinders is described by A. H. White[117] and an arrangement patented by Pope[118] provides for a very long exposure of the paper after passing over each pair of cylinders, by mounting each of the upper range of cylinders vertically above the corresponding cylinder of the lower range.

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[111] *Paper Making*, 36, 1917, 145; *J.*, 1915, 592.

[112] S. Webb. U.S. Pat. 1,201,402; *J.*, 1916, 1215.

[113] U.S. Pat. 1,193,613; *J.*, 1916, 961.

[114] Eng. Pat. 4186/1915; *J.*, 1916, 418.

[115] Eng. Pat. 17814/1915; *J.*, 1917, 288.

[116] Eng. Pat. 3286/1915; *J.*, 1916, 303.

A rather attractive proposal for supplying steam to the drying cylinders is made by W. A. Aitken.[119] The cylinders are divided into two or more groups, each with separate inlet and discharge mains. The whole of the steam required for drying is admitted to the last group at the dry end of the machine and passes through each group in series to the wet end, the discharge main of each group being connected with the inlet main of the next, which is situated at a higher level so that drainage of condensed water can take place. A device for controlling the supply of drying steam by the electrical conductivity of the moist paper has been patented by E. P. Butts.[120] The paper passes between a pair of rollers connected with a source of electricity and the current which passes through the paper operates the steam valve through an electro-magnet.

Waste Paper.

Owing to the scarcity of raw materials, increased attention has been turned to the cleansing of printed waste paper. Mild alkalis and soap are generally employed for this purpose, but Rohm and Haas[121] propose the use of proteolytic and lipolytic enzymes such as those obtained from the pancreatic gland of animals or from the papaw fruit or castor beans.

In a process patented by the Neo-Cellulose Co.,[122] the impurities loosened by soap are collected and separated by creating a foam which is rendered stable by the addition of a fat or vaseline. An apparatus devised by the same inventors[123] consists of a rotating drum with breaking and conveying blades depending from the horizontal axis. The first part of the drum, in which the paper is broken up to a pulp, has solid walls, the latter part having perforated walls, so that when the pulp has assumed the form of a rolling coherent mass it may be washed by sprays of water directed on it from inside. Another type of drum machine[124] has helical convolutions on the inside forming an open channel for the travel of the material, with obstructions which impede the passage of unreduced pieces and return them up the drum. The principle of washing waste paper stock by jets of water directed on the reverse side of a wire cloth with the moving pulp on the other side is patented by S. Milne.[125] A new type of pulping machine has been described, containing a series of propeller blades revolving at such a high speed that a drawing action is exerted against the inertia of the paper in the suspending liquid, and the component fibres of the paper are drawn apart.[126]

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[117] U.S. Pat. 1,232,141, *J.*, 1917, 960.

[118] U.S. Pat. 1,214,712, *J.*, 1917, 334.

[119] Eng. Pat. 106,228/1916, *J.*, 1917, 708.

[120] U.S. Pat. 1,212,014, *J.*, 1917, 212.

[121] Ger. Pat. 287,884; *J.*, 1916, 357.

[122] Eng. Pat. 105,055/1916 *J.*, 1917, 868, and Eng. Pat. 108,434/1917; *J.*, 1917, 1045.

Special Papers.

Filter paper.—F. J. Bevan and W. Bacon[127] give some general information on the subject of English filter papers from which it would appear that before the war some 500,000–600,000 lb. of foreign chemical filter paper was imported into this country and that the English manufacturers have successfully solved the problem of making this class of paper in the highest qualities. Success has also attended the manufacture of filter pulp for brewers' use.[128] In both these cases cotton is the most suitable raw material and the purity and soundness of the fibre the most important consideration. According to Gawalowski[129] the purification of filter paper by dilute hydrofluoric acid is easily effected as regards the silica but the lime and iron oxide are somewhat resistant to this acid.

Roofing felt.—Standards for the composition and properties of roofing felt board have been adopted in Germany[130] and the use of ground bark wastes in the manufacture of these boards and other specialties is recommended by O. Kress.[131] Promising results have been obtained by screening and refining spent tannery bark or pulp-wood bark and mixing the product with a proportion of standard fibre pulp; wall papers, wall boards, and fibre tubes have been made from these mixtures.

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[123] Eng. Pat. 104,952/1916; *J.*, 1917, 544.

[124] Fiske. Eng. Pat. 103,370/1916; *J.*, 1917, 288.

[125] Eng. Pat. 107,410/1916; *J.*, 1917, 959, and Eng. Pat. 109,594/1917; *J.*, 1917, 1174.

[126] Wade. Eng. Pat. 3,702/1915; *J.*, 1916, 833.

[127] *Analyst*, 1916, **45**, 159; *J.*, 1916, 733.

[128] Foster. *J. Inst. Brewing*, 1916, **22**, 413; *J.*, 1916, 1170.

[129] *Z. anal. Chem.*, 1915, **54**, 503; *J.*, 1916, 250.

[130] Marcusson. *Mitt. K. Materialpruf.*, 1916, **34**, 40; *J.*, 1916, 1100.

A new method of making roofing sheets is described by Woodley,[132] according to which moist pulped stock is incorporated with an asphaltic binder by forcing the mixture repeatedly through perforated plates until homogeneous and then rolling it out into sheets.

Moisture-proof paper. In making vessels of paper which has to be rendered moisture-proof, *e.g.*, by waxing the finished article, the vessels are made up by uniting two sheets of paper by an adhesive which is immiscible with the proofing agent, so that the proofing agent cannot penetrate right through the paper.[133]

Ornamental paper. Paper ornamented by deeper and lighter shades of colour on its surface is made, according to a patent by The Strathmore Paper Co.,[134] by applying a colouring or decolorising medium to the uneven surface of the web on the wire by means of a pressure roller. The uneven surface is produced by putting the first suction box out of action so that the pulp tends to bank up and become crushed by the dandy roll; the colour may be sprayed on to the upper couch roll, and thus applied to the paper, being displaced from the elevated portions of the sheet and concentrated in the depressions.

Vulcanised fibre. Plates of hard vulcanised fibre are softened by steeping in a solution of zinc chloride (1 : 5), dried in the air, impregnated with an emulsion of oil and water and subsequently with oil alone. The treated plates are dipped in melted paraffin wax or a solution of sodium silicate. They are flexible and can be used as a substitute for sole-leather.[135] A new modification of vulcanised fibre is prepared by impregnating ordinary vulcanised fibre with a solvent which may be used for displacing the moisture from the washed fibre. Alcohol is a suitable displacing medium; the alcohol is then itself displaced by a proofing or softening substance which is soluble in the alcohol. For instance, an intermediate "bakelite" product may thus be introduced and then fixed as a solid condensation product by heating, or else a modified oil, such as sulphonated oil, may be used to impart flexibility.[136]

[131] *J. Ind. Eng. Chem.*, 1916, **8**, 883; *J.*, 1916, 1105.

[132] Eng. Pat. 8815/1915; *J.*, 1916, 1009.

[133] C. A. Bickett. U.S. Pat. 1,203,302; *J.*, 1916, 1256.

[134] Eng. Pat. 108,340/1916; *J.*, 1917, 1045.

[135] T. Oye. Eng. Pat. 105,033/1916; *J.*, 1917, 514.

[136] J. McIntosh. U.S. Pats. 1,236,460 and 1,236,461; *J.*, 1917, 1092

Paper tubes.—Experiments have been made by Rudeloff[137] on the mechanical properties of various commercial types of paper tubes. These tubes differ in quality and power of resistance according to the substance with which they have been cemented, coated, or impregnated; they are intended to serve as conduits for gas or water. They are only $\frac{1}{6}$ to $\frac{1}{10}$ the weight of lead pipes and resist [illegible] 4 times the internal pressure for equal diameters. None of the paper tubes, however, could be regarded as permanently capable of resisting the softening action of water. A type of tube called "Pertinax" is made by impregnating paper with synthetic resin and rolling up under tension; these tubes would appear to be suitable for oil conduits. Paper tubes show a sufficiently good tensile strength but low compression strength; the modulus of elasticity is low and the resistance to bending stresses very poor; they cannot be regarded as adapted for structural purposes.

Fireproof writing paper.—R. G. Myers[138] has made experiments with pulps prepared from chrysotile fibre together with precipitates of metallic compounds. The best papers as regards quality were prepared from pulps containing precipitated hydroxides, arsenites, silicates, and tungstates, particularly one containing a large excess of magnesium arsenite in an alkaline mixture. As the result of firing for 10 hours at 900°–1,000° C., it is concluded that no paper composed of incombustible substances containing molecular water can be made fireproof, but several can be exposed to a dull red heat for 1 or 2 hours. For fireproof inks, ferric, chromic, and cobaltous nitrates and chlorides give satisfactory results.

Paper Testing and Analysis.

An agreement has been arrived at between the American Paper and Pulp Association and the Association of Wood Pulp Importers regarding the sampling and testing of wood pulp for moisture.[139] The samples are taken by boring discs, 4 inches in diameter, with a special auger. Directions are given for taking the samples in different positions on the bales and at definite intervals in depth. Rules for controlling the percentage retention of mineral loading in paper on the machine are given by Plumstead.[140] Samples are taken at different stages in the manufacture and the loss of filler at each point is determined by drying and incinerating.

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[137] *Mitt. K. Materialpruf.*, 1916, **34**, 61; *J.*, 1917, 592.

[138] *J. Ind. Eng. Chem.*, 1916, **8**, 888; *J.*, 1916, 1105.

[139] *Paper Making*, 1916, **35**, 10; *J.*, 1916, 172.

[140] *Chem. Eng.*, 1916, **23**, No. 2; *J.*, 1916, 629.

Conditions for the determination of the wet strength of paper have been proposed by E. O. Reed.[141] These are necessarily chosen quite empirically, as the wet strength varies with the temperature of the water and time of immersion. Strips are steeped for 20 mins. in water at 70° F. (21° C.) and then immediately broken in the testing machine. To obtain a high wet strength the paper should be made from long fibre pulp beaten "wet" and well felted and sized so as to give the maximum resistance to the penetration of water.

Three "direct" tests which have been developed at the Prussian Testing Institute for measuring the suitability of paper for certain specific purposes, are worthy of notice. W. Herzberg[142] describes an arrangement of apparatus for determining the permeability to air of paper clamped firmly between two metal flanges and subjected to a constant difference of pressure corresponding to 10 cm. of water. The volume of air aspirated through the paper while maintaining this difference of pressure is calculated in terms of litres per min. per 100 sq. cm. of area. The results afford an effective measure of the porosity of the paper, and hence of its suitability for airtight wrappers; for instance, vegetable parchments and greaseproofs have a permeability of only 0·1, which is so low that it may be regarded as equivalent to zero for purposes where no difference of pressure exists.

A method of a similarly direct order for the determination of the permeability to heat of fabrics and paper is described by O. Bauer.[143] The heat passing through the uninsulated bottom of an insulated copper vessel containing water at 100° C. to the junction of a thermo-electric element placed beneath it, is measured with and without the interposition of the material under examination, observations being taken at intervals of two minutes over a period of 90 mins. There is no definite relation between the heat protective value of a material and its nature, thickness, specific gravity, &c., and the relative values of different fabrics can only be ascertained by actual tests.

A third direct method, described by C. Bartsch,[144] relates to the determination of the grease-resistance of greaseproof papers. A layer of fat, 1 mm. thick and 25 sq. cm. in area, is smeared over the paper by using a zinc template with a square hole, and the treated paper is placed on a sheet of white note paper, between two glass plates loaded with a 500 grm. weight, for one hour. Different fats have different penetrating powers and lard is recommended as a standard.

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[141] *J. Ind. Eng. Chem.*, 1916, **8**, 1,003; *J.*, 1916, 1,214.
[142] *Mitt. K. Materialpruf.*, 1915, **33**, 142; *J.*, 1916, 38.
[143] *Mitt. K. Materialpruf.*, 1915, **33**, 290; *J.*, 1916, 922.
[144] *Mitt. K. Materialpruf.*, **1915**, **33**, 411; *J.*, 1916, 923.

The results are classified in groups according to the number of stains observed on the white paper. Greaseproof paper should show only very few (not more than 15) small, practically isolated stains under these conditions.

The influence of humidity on the physical properties of paper has been studied by O. Kress and P. Silverstein,[145] also by R. Campbell.[146] The conclusions arrived at concerning the decrease of tensile strength and increase of tensile stretch, when the relative humidity of the atmosphere is increased, confirm previously recorded observations. The folding strength of paper tends to increase with the humidity up to a maximum at about 80% humidity, more or less, according to the nature of the paper. After this point, a further increase in humidity causes a sharp drop in the folding resistance. The resistance to ink penetration falls considerably as the humidity is increased.

O. Kress and G. C. McNaughton[147] describe the construction and manipulation of the Ives tint photometer as a means for the colour analysis, in terms of red, green, and blue, of tinted white and coloured papers as determined by reflected light. The instrument is quite satisfactory for this purpose and gives numbers applicable in practical colour matching. Experiments were also made with Ingersoll's "glarimeter" to determine the effect of calendering; this instrument shows the percentage of light reflected where the angle of incidence is equal to the angle of reflection in comparison with the total reflected light. The results show that whilst the glarimeter might be of value in determining the finish of white papers, it is not suitable for coloured papers of different hues and intensities.

M. Yano[148] has studied in microscopic cross-sections the penetration of coloured printers' ink varnish into papers of different textures, the penetration varying with the fineness of texture. If the printed paper be dried at too high a temperature the varnish penetrates too quickly and the pigment separates on the surface and rubs off; this may be prevented by the addition of manganese borate. Rosin size does not impede the penetration of printing ink but gelatin sizing prevents it. An excess of mineral loading fills up the pores of the paper and prevents the penetration of the varnish.

The determination of the cupric reducing value of cellulose according to Schwalbe's method, taking all the minute precautions necessary to avoid incidental errors, is a very complicated operation.

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[145] *J. Ind. Eng. Chem.*, 1917, **9**, 272; *J.*, 1917, 449.

[146] *J. Ind. Eng. Chem.*, 1917, **9**, 658; *J.*, 1917, 923.

[147] *J. Ind. Eng. Chem.*, 1916, **8**, 711, and 1917, **9**, 282; *J.*, 1917, 149.

[148] *J. Chem. Ind.*, *Tokyo*, 1917, **20**, 219; *J.*, 1917, 868.

Freiberger[149] has enumerated certain further precautions required for obtaining trustworthy results. Both the alkaline tartrate and the copper solutions should be freshly prepared and the sodium hydroxide should be made from metallic sodium and dissolved in a clean iron vessel. Rubber stoppers must not be used and the introduction of sodium silicate in the distilled water must be guarded against. The Fehling's solution must be poured off the cellulose immediately the boiling operation is completed and the cellulose washed a few times by decantation before filtering the solution, preferably through paper. In this way the further deposition of cuprous oxide which takes place when dilute Fehling's solution is heated, is prevented. It must be admitted, however, that the large number of complicated precautions and the special apparatus now required to obtain trustworthy results by the Schwalbe method detract from its practical utility for technical purposes, making it more suitable for a University laboratory. Undoubtedly a modification in the direction of simplicity and rapidity is required if the original object of the test is to be maintained.

R. S. McBride and J. A. Scherrer[150] have determined that the majority of chemical filter papers contain reducing substances which have an appreciable influence when a delicate permanganate titration has to be made after filtration, especially with hot titrations. The reducing matter is readily soluble in aqueous media and most of it is removed if the filter be subjected to a preliminary washing with 25 c.c. of the reagent which is to be used in the filtration; the error is then negligible and is no greater even if the titration be made in presence of the paper.

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[149] *Z. angew Chem.*, 1917, **30**, 121; *J.*, 1917, 707.

[150] *J. Amer Chem. Soc*, 1917, **39**, 928, *J*, 1917, 736.

BLEACHING, DYEING, PRINTING AND FINISHING.

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THIS branch of chemical industry has, like other branches, been affected by the war. The nature of the productions of many works has been entirely changed; the scarcity of certain chemicals has caused rigid economy or the employment of substitutes; and the interference with the dyestuff supply has caused many difficulties. In fact, it is remarkable that the industry has been kept going, in spite of all the difficulties, and it would not be to the national advantage to explain in detail the devices adopted to overcome the difficulties.

Various new machines have been described, but, in the cases where full details have been given, there does not seem to have been any revolutionary change. Many of the inventions have been devised for special classes of work. As in most other industries, not engaged directly in the production of munitions of war, less research than usual has taken place; owing to the scarcity of labour and other troubles, the managers and technical men have required all their energies to keep the works going, and have found little time for experiment and the development of new processes. In the United States, however, a large amount of research in textile chemistry has been performed in recent years.

This branch of applied chemistry has always attracted a number of chemists, perhaps more than most other branches of chemical industry. Whether these chemists have been of the first rank may be disputed in some quarters, but certain it is that, in an unostentatious way, they have brought the industry to a high degree of scientific development. This development has also been assisted by the connection between the industry and the aniline dyestuff industry, which is probably the most highly developed, in a scientific sense, of all industries. Yet it must be admitted that among managers and technical men employed in the industry there is usually a reticent feeling, a feeling which keeps them from discussing their successes and troubles with others outside the works. They always appear extremely anxious not to divulge anything of value, and in some cases are given strict injunctions by their superiors to that effect. "Secrets," however, leak out, and it is in the interests of the industry as a whole that discussions on scientific and technical points should take place.

During the period under review it is gratifying to note that research in the industry has received official support. Committees have been formed by the Society of Dyers and Colourists, problems selected and grants in aid of research on these problems made; a number of problems have been considered by committees appointed by the Textile Institute; and this Society has received grants in aid of a research bearing on the technical development of the industry under review. There seems to be a public awakening concerning the necessity for the application of scientific research to the textile and subsidiary industries. A large amount of work is awaiting execution, but it will be necessary to see that it is begun on a right basis if the industries are to obtain the full benefit. Moreover, it is well to remember that such work will depend for its success upon the progress of pure chemistry, as will be explained later.

It is a remarkable fact that in different works similar results are achieved by different processes. Nobody seems to understand why the variety of processes are used, except that they have been found successful for years. One printworks uses lime boiling for preparing the cloth; and another works, not many hundred yards away, uses caustic soda boiling. Because both methods give satisfactory results no further attention is paid to the matter; in industry, results, not methods, are considered provided economy is achieved. The processes mentioned are not yet fully understood, and it is in matters of this kind that research is required. It must not be thought, however, that a scientific chemist entering the industry can solve all the difficulties encountered. Textile chemistry is one of the most difficult branches of technical science, and long and painstaking research is required before any conclusions whatever can be arrived at.

The reason that textile chemistry is so difficult and depends so much on experience, is because the chemist is dealing with substances or mixtures of substances, the chemical constitutions of which are unknown. For instance, raw vegetable fibres contain as a rule: (1) cellulose, concerning which substance a large amount of research work has been performed, but no definite ideas formed as to its constitution; (2) waxes, the thorough investigation of which has only recently been commenced; (3) proteins, the chemistry of which is extremely complex, and the constitution far from determined;

(4) pectic matter, concerning which little is known; (5) colouring matters of undetermined constitution; and (6) mineral matter.[1] This collection of substances of unknown chemical constitution serves to indicate why the industry was founded on empiricism rather than on a scientific basis. The bleacher, dyer, and printer of textiles first aims at separating the non-cellulose constituents of the fibre from the cellulose; the bleacher's duty is merely to make this separation in the best and cheapest way he can and with the least possible injury to the cellulose of the fibre. The methods used are the results of accumulated experience but chemical knowledge is being found of greater and greater assistance. Important work has recently been performed on the constituents of textile fibres, and progress in the textile industries will depend on investigations of the natures of the waxes, proteins, and pectins of plants. For instance, recent work on the action of chlorine on proteins is of interest, and serves to show the connection of an important industry with a branch of biological chemistry.

BLEACHING.

An important method of bleaching has been outlined by Levine,[2] who showed that the ether-soluble and nitrogenous constituents of cotton cloth can be removed by the action of certain bacteria in a nutrient solution containing certain inorganic salts; the cloth is merely immersed in the solution instead of being scoured with lime or caustic soda. Röhm[3] treats raw cotton with a 0·1 % solution of pancreatin at 20°-40° C. for some hours and then bleaches in the usual way. He later[4] protects the use of this solution for the cleansing of other articles than textiles, and Kwaisha[5] uses the proteolytic enzymes in the juice extracted from the bodies or cocoons of insects or silkworms in order to dissolve the sericin and loosen the fibres of silk. The use of enzymes in the bleaching of cotton is of interest; previously they had been used extensively to remove the size from cotton cloth before scouring, but in this new development the action of the enzyme is taken further, namely, to eliminate the fatty matter and the proteins from the fibre. The following questions, however, arise: (1) Can all the impurities be removed without resorting to ordinary scouring, (2) how does the cost of the enzyme and nutrient solutions compare with that of ordinary scouring solutions; and (3) if lime salts are present in the nutrient solution is it necessary to treat with acid after the action of the enzymes, in order to eliminate the lime? It must not be forgotten that some enzymes attack cellulose, and unless this action be prevented the methods of cleansing mentioned may have an effect on the strength of the fibre, just as over-retting rots linen. It might be difficult to stop the action when the non-cellulose constituents of the fibre have been removed and the cellulose itself not attacked. Caustic soda boiling is found to have no deleterious action on cellulose, even on boiling with that solution for 10 hours under pressure. Moreover, weak caustic soda solution is an ideal cleansing agent for textiles, since it removes the waxes by saponification; it is the best hydrolysing agent for proteins, and it eliminates the pectic matter from the fibre. Perhaps the most important point in bleaching is to have a safe method of separating the cellulose. Only safe methods can survive. A method might be very scientific and economical, but if it results in an occasional lot of goods being "tendered," then the economy of the method disappears and the method cannot survive. In fact, methods which require careful scientific control in order to save tendering do not commend themselves to bleachers; methods which are not risky and can be entrusted to workmen not scientifically trained are preferred. Some time ago a method of bleaching cotton in one operation was described. The cotton was heated in the kier along with the scouring liquor, to which was added a certain quantity of a manganese salt, and air was passed through the goods while in the kier. The idea was to oxidise the manganous salt by the air, the oxidised salt being reduced to its original state by oxidising the non-cellulose constituents of the fibre, and thus by a cycle of operations oxidising, and therefore bleaching, the cotton during the scouring operation. The method is ideal from the chemical standpoint. The writer has not heard if this process of bleaching has survived, but thinks the point mentioned above, namely, risk of tendering, would sooner or later cause its discontinuance.

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[1] Barnes (*J.*, 1916, 1191) has shown that raw cotton gives as much as 1 % of ash on incineration and the variable mineral content affects the properties of the fibre during dyeing and other operations.

[2] *J., Ind. Eng. Chem.*, 1916, **8**, 298-302; *J.*, 1916, 687.

[3] Eng. Pat. 100224, 1916; *J.*, 1916, 1057.

[4] Eng. Pat. 107191, 1916; *J.*, 1917, 955.

[5] Eng. Pat. 106503, 1917; *J.*, 1917, 959.

The cause of the yellowing of bleached cotton on steaming and storing has lately been discussed. Levine[6] confirms Hebden's[7] conclusion that the turning yellow is partly due to nitrogenous impurities; but he also finds that the ether-soluble impurities have some action.

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[6] *J. Ind. Eng. Chem.*, 1916, **8**, 298–302; *J.*, 1916, 687.

[7] *J.*, 1914, 959.

Freiberger[8] states that cloth bleached with cold hypochlorite solution and then soured did not keep so well on storing as the same cloth bleached in a warm alkaline and then a warm acid bleaching bath. The present writer[9] found that any of the residual non cellulose constituents of fibre had the effect of causing yellowing on storing, and that the only method of preventing this fault was by proper scouring before bleaching.

That scouring increases the strength and elasticity of cotton yarn has been confirmed.[10] If, however, the yarn was not properly scoured before treatment with the hypochlorite solution, there was an actual loss in strength.[11] Seel and Sander[12] found no structural modification of cotton and linen, when viewed under the microscope, after treating with acids, alkalis, and oxidising agents. Wool, however, was affected by alkaline boiling, and soap instead of soda ash was recommended for this work.

The Bleaching Action of Hypochlorite Solutions.

Korselt[13] claims the use of hypochlorite solutions of gradually increasing, instead of decreasing, concentration. This method may produce a good white but certainly not a cheap one, considering the amount of strong hypochlorite which is retained by the cloth and lost in the subsequent washing process. Briggs[14] discusses the economy of hypochlorites in bleaching operations. The theory of the bleaching action of hypochlorites has been the subject of much controversy,[15] [16] but it now seems to be established that their bleaching action is due to (1) the direct production of nascent oxygen by the hypochlorites, and (2) the production of nascent chlorine by the action of the hypochlorous acid present in solution on the chlorides also present. A number of observations bearing on this discussion have recently been made. It was found[17] that very dilute solutions of hypochlorites decompose slowly, the velocity of decomposition being apparently represented by a portion of a rectangular hyperbola. It had previously been shown[18] that the velocity of the bleaching action of such solutions could be represented in a similar manner. Ricci[19] states that the addition of chlorides, as a rule, has little effect on the stability of hypochlorites, although under some circumstances the addition has an appreciable effect on the stability and bleaching efficiency of the solutions.[20] A. Smith[21] supports previous work,[22] showing that bleaching powder solution and sodium hypochlorite solution produced by the electrolysis of common salt solution give identical results in bleaching processes. The pink colour of hypochlorite solutions, sometimes noticed in laboratory experiments, but seldom nowadays in commercial liquors, has been attributed to the presence of ferrates; but further work has shown[23] that it is due to permanganates, the manganese being derived from the bleaching powder. The present writer had noticed this pink colour in hypochlorite solutions in contact with manganese compounds, such as manganese dioxide.[24] It is interesting to note the use of a mixture of bleaching powder and boric acid as a powerful antiseptic in surgery. This mixture had previously been used by chemists to prepare hypochlorous acid by distillation, and the present writer showed[25] by adding boric acid to hypochlorite solutions, that an extremely active bleaching solution was produced.

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[8] *Z. angew. Chem.*, 1916, **29**, 397–400; *J.*, 1916, 629.

[9] "Dyeing in Germany and America," second edition, Longmans, Green and Co., 1916.

[10] F. P. Jacusco, *J. Soc. Dyers and Col.*, 1917, **33**, 31–38; *J.*, 1917, 288.

[11] See also Higgins, *J. Text. Inst.*, 1916, 38.

[12] *Z. angew. Chem.*, 1916, **20**, 261–265; *J.*, 1916, 886.

[13] Ger. Pat. 287240, 1913; *J.*, 1916, 174.

[14] *J.*, 1916, 799.

[15] Higgins, *J.*, 1913, 350, 359, 1064, 1153; 1914, 785, 1152.

[16] Taylor, *J.*, 1914, 38.

[17] L. Vallery, *Comptes Rend.*, 1916, 326; *J.*, 1916, 378.

[18] Higgins, *J. Chem. Soc.*, 1913, **103**, 1816; *J.*, 1913, 1064.

Degree of Bleaching of Cellulose.

Many methods of determining what is called the degree of bleaching of cellulose fibres have been described from time to time, but this work has been of little interest to the practical bleacher, he contents himself with the usual strength tests, and only examines the material for the so called oxy-and hydro-cellulose in cases of decided weakness of the fibre. The "copper value" of Schwalbe has been much discussed, but Freiberger[26] states that certain precautions are necessary in applying this method. Further, he[27] attempts to classify the whites of bleached goods by observing the stains they produce with waste bowking liquors. Haller,[28] however, points out that such a method of distinction is only applicable to goods bleached by the same system of bowking and bleaching. He ought to have further added that such a method of comparison could only possibly be of use when the same cloth was used in all the tests.

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[19] *J*, 1915, 714

[20] Higgins, *J*, 1911, 185.

[21] *J*, 1916, 185.

[22] Higgins, *loc cit*

[23] Elledge, *J Ind. Eng Chem*, 1916, **8**, 780, *J*, 1916, 1013.

[24] *J*, 1913, 359.

[25] *J*, 1914, 1152.

[26] *Z. angew. Chem*, **1917**, **30**, 121-122, *J*, 1917, 707

[27] *Färber-Zeit.*, 1915, **26**, 319-321; 1916, **27**, 26-27; *J*, 1916, 629.

The behaviour of the waxes of textile fibres during the bleaching process is discussed by the writer,[29] and the efficacy of the lime boil explained.[30] Because of the difficulty of removing the natural waxes during bleaching, James Burt-Marshall, Ltd., and S. H. Higgins[31] extract the waxes by solvents before the bleaching process. Apparently with a similar intention Peckham[32] boils the cloth in a soap solution containing benzol instead of scouring in the usual way, and, further, a solution containing potash soap, carbon disulphide, and olein has been suggested for removing grease from fabrics.[33] A recent research on pectic matters[34] is of interest to bleachers, and the removal of pectic matter from vegetable fibres by means of a hot aqueous solution of hydrochloric acid has been protected.[35] In bleaching with an alkali peroxide, a claim is made[36] for heating the bath immediately to 85° C. to produce a better white in a shorter time. To prevent the flocculation of calcium soaps in washing baths, the addition of a soluble colloid, *e.g.*, glue, albumin, etc., is protected.[37]

In a paper on bleaching faults, J. F. Briggs[38] discusses most of the troubles with which bleachers have to contend, and a paper by Budde[39] is of interest to those bleachers who are troubled with river pollution. On exposing bleached cotton to the action of the light of a Cooper-Hewitt lamp it was found to be "tendered" and apparently partially changed to "oxycellulose."[40]

Use of Nitre Cake in Bleaching

Owing to the war, acids have been costly and scarce. Nitre cake has been used in many cases in place of sulphuric acid and of hydrochloric acid for "souring" textiles. Except in certain cases, such as lime souring, it has been found a good substitute, and even in the case mentioned it has been used, with advantage, after the goods have been well washed. Troubles of dissolving the cake and testing its acidity have been mentioned; special tanks have to be used, and the solution tested volumetrically.[41]

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[29] *J.*, 1914, 902.

[30] See also Higgins, *J. Text. Inst.*, 1916, **7**, 30.

[31] Eng. Pat. 102892, 1916; *J.*, 1917, 211.

[32] *Met. and Chem. Eng.*, 1916, **4**, 160; *J.*, 1916, 303.

[33] S. Dyson and J. Dyson and Co., Ltd. Eng. Pat. 10311, 1913; *J.*, 1916, 887.

[34] S. B. Schryver and D. Haynes, *Biochem. J.*, 1916, **10**, 539–547; *J.*, 1917, 577.

[35] B. Leech. Eng. Pat. 104202, 1916; *J.*, 1917, 451.

[36] Deutsche Gold-und Silber-Scheide Anstalt, Eng. Pat. 10916, 1915; *J.*, 1916, 925.

[37] Farbenfabr. vorm. F. Bayer und Co., Ger. Pat. 294028, 1914; *J.*, 1916, 1153.

[38] *J.*, 1916, 78.

[39] *J.*, 1916, 404.

[40] Dorée and Dyer, *J. Soc. Dyers and Col.*, 1917, **33**, 17–19; *J.*, 1917, 211.

The Action of Acids on Cotton.

The tendering action of acids on cotton has been investigated by M. Fort and F. Pickles,[42] and discussed by J. F. Briggs[43]; cellulose does not form compounds with acids, and with mixtures of acids selective adsorption was only pronounced at high concentration.[44] The tendering effect of acids on cotton was found[45] to increase with the length of time of contact and was reduced by washing with water or alkali. Zänker and Main[46] found that a mixture of Glauber's salt and acetic acid caused tendering of cotton, but that this was the best mixture to use in dye baths for union goods.

Of interest to both bleachers and dyers has been the trouble experienced by many bleachers of cotton piece goods woven with coloured borders. Many new dyestuffs have been used for dyeing the yarns for these coloured borders, in some cases "bleeding" into the white cloth resulted during the scouring process. The new dyestuffs have been fairly fast to the usual tests, except the test mentioned, and when once the colours have "run" the bleacher finds it impossible to correct the fault. To prevent the bleeding of vat colours, padding the cloth with caustic soda solution, to which non-oxidisable salts have been added to prevent the solution of the colour, and allowing the goods to lie some time before the process of bleaching, has been protected.[47]

DYEING.

The troubles to dyers caused by the interference with the supply of dyestuffs have been discussed by Whittaker.[48] Wood colours have been more used than formerly, although previous to the war they were used in large quantities by some yarn dyeing works.[49]

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[41] *Chem. Trade Journ*, Jan 8, 1916, *J.*, 1916, 109, J R Hannay, *J. Soc. Dyers and Col*, 1916, **32**, 65 66, *J.*, 1916, 48; P Bean, *J.*, 1916, 1153. See also *J*, 1917, 1216A. [42] *J*, 1916, 38 [43] *J*, 1916, 78

[44] A Leighton, *J. Phys Chem*, 1916, **20**, 188-194, *J*, 1916, 464

[45] H Wilkinson, *J Soc Dyers and Col*, 1917, **33**, 148 151, *J*, 1917, 707.

[46] *Färber-Zeit*, 1916, **27**, 355, *J*, 1917, 708

[47] J Graf, Ger Pat 288751, 1914; *J*, 1916, 419

[48] *J.*, 1916, 783, 1201.

[49] "The dyeing value of some natural Indian dyestuffs." Srivastava, *Agric. J.* India, 1916, 53-64, *J.*, 1916, 961, "Cutch in Burma," *J*, 1917, 208, "Dyeing materials in the Philippines, *J. Roy. Soc Arts*, 1917, **65**, 553; *J.*, 1917, 706.

Of recent years there has been an inclination towards the production of fast dyes; fastness has received more consideration than hitherto. The use of vat dyestuffs has extended, and as pointed out in Vol. I of these Reports, there has been a marked activity in the production of new shades by the developing of azo-dyestuffs on the fibre. Fast grey shades are produced on cotton by the oxidation on the fibre of di-β-naphthyl-4.4′-diaminodiphenylaminesulphonic acid[50]; clear red to dark blue shades by impregnating the fibre with a sodium carbonate solution of arylides of 6-hydroxy-2-naphthol-3-carboxylic acid, then heating with a solution of an unsulphonated diazo compound[51]; Turkey red shades by coupling an aromatic diazo compound with 2.3-hydroxynaphthoylaminothiazole[52], fast black dyeings by coupling an arylide of 2.3-hydroxynaphthoic acid and a diazotised *asym.*-dialkyl-*p*-diaminoazo compound[53]; and yellow to black shades by impregnating the cloth with a sodium carbonate solution of 2.3-hydroxynaphthoylaminonaphtholsulphonic acids and then treating with unsulphonated diazo compounds[54]. Further development of the use of formaldehyde for these fixations is shown in the production of fast red to blue shades by treating on the fibre with formaldehyde the dyestuffs obtained by coupling tetrazotised diamines with one molecule of an aminonaphtholsulphonic acid and one molecule of an amino-substituted derivative of 2.5.7-aminonaphtholsulphonic acid containing a free amino group[55].

Other examples of dyestuffs produced on the fibre are a brown shade by oxidising salts of aniline and its homologues mixed with an aromatic hydroxy compound containing no nitro, nitroso, or amino group, *e.g.*, a phenol[56]; an aniline black, said to be unaffected by sulphur dioxide, by the interaction, at a high temperature, of aniline, a diamine and chloric acid, with or without another mineral acid containing oxygen, but without salts of copper, iron, manganese, vanadium or chromium[57]; a deep black on wool, by treating with a solution of a mono- or polysulphonic acid and of a *p*-amino- or *p*-arylamino-aryl-β-naphthylamine, then chroming[58]; fast khaki shades on wool by baths containing dihydroxy- or aminohydroxynaphthalenesulphonic acids and copper salts[59]; and khaki shades on animal or vegetable fibres by immersing them in bichromate solution, and then in a solution of a substance obtained by melting together four parts of a *m*-diamine with one part of a *p*-phenol.[60]

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[50] Farbenfabr vorm F Bayer und Co, Ger Pat 296142, 1916, *J*, 1917, 597.

[51] Farbenfabr vorm F Bayer und Co, Ger. Pat 294798, 1914, *J*, 1917, 81

[52] Farbw vorm Meister, Lucius, und Bruning, Ger Pat. 294780, 1914; *J*, 1917, 81

[53] Chem Fabr Griesheim-Elektron, Eng Pat 100804, 1916, *J*, 1916, 188

[54] Farbenfabr vorm F Bayer und Co, Ger. Pat 296559, 1914, *J*, 1917, 594

[55] Farbenfabr vorm F Bayer und Co., Ger Pat 295072, 1914, *J*, 1917, 213.

[56] J F Moseley and E McCardell, Eng Pat 105349, 1916, *J*, 1917, 594

[57] Ehrenzweig, Ger. Pat 291955, 1913, *J*, 1916, 834

[58] Farbenfabr vorm F. Bayer und Co, Ger Pat 291021, 1914, *J*, 1916 834.

The use of titanium stannate or tanno-oxalate as a mordant has been described.[61] A number of shades on animal fibres are said to be produced by the action of metallic salts in the presence of nitrites and of an acid.[62] In the dyeing of wool and silk with vat colours the addition to the bath of a small amount of alkali and of the hydroxide of a heavy metal has been protected.[63] For the dyeing of tussah silk Sen[64] recommends the methods used for dyeing wool, since this fibre resembles wool in its behaviour towards dye solutions. The interaction of certain dyestuffs with copper during dyeing operations has been pointed out by J. R. Hannay[65] and the use of acetic acid in place of sulphuric acid for after-chroming has been recommended in order to prevent the partial destruction of the dyestuff by oxidation.[66] O. Diehl[67] suggests the use of a slightly acid alizarin dyebath and rapidly raising the temperature to complete the dyeing within a quarter of an hour. Sen[68] has described a method of producing aniline black on wool.

Further work has been done by E. Lodge[69] on the application of sulphide dyestuffs to animal fibres, sulphites and hydrosulphites being used for the reduction of the dyestuff, and excess of alkali in the dyebath avoided so as not to impair the strength of the fibre. Sen[70] adds Turkey red oil to the bath to improve penetration, and describes methods of producing sulphide dyestuffs on wool. The tendering of fabrics which have been dyed with sulphide dyestuffs has been further investigated. The dyestuffs are said gradually to liberate sulphur, which in the course of time becomes oxidised to sulphuric acid and thus causes the "tendering" of vegetable fibres. Various methods have been described and patented for preventing this defect of sulphide dyestuffs. For instance, treatment of the dyed fabric with a bath of sodium acetate, thus leaving a small quantity of this salt on the fibre, has been used; if sulphuric acid be afterwards developed, it acts on the acetate, liberating acetic acid, which does not injure the fibre. It is said[71] that fabrics dyed with black sulphide dyestuffs, which will withstand heating to 140° C. for one hour without tendering, may be stored with safety. To prevent the "tendering" of the cotton of union goods dyed with sulphide dyestuffs, an after-treatment of the fabrics with ammonium salts and chromates has been patented. This treatment also dyes the wool.[72]

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[59] Farbenfabr. vorm. F. Bayer und Co., Ger. Pat. 291456, 1914; *J.*, 1916, 834.

[60] R. Vidal, Eng. Pat. 1024, 1916; *J.*, 1916, 1357.

[61] Barnes, *J. Soc. Dyers and Col.*, 1916, **32**, 141-142; *J.*, 1916, 630.

[62] E. and G. E. F. Lodge, *J.*, 1916, 409.

[63] R. Wedekind, Ger. Pats. 287042, 1913 and 289314, 1912; *J.*, 1916, 419.

[64] *J. Soc. Dyers and Col.*, 1916, **32**, 243-244; *J.*, 1916, 1106.

[65] *J.*, 1916, 36.

[66] E. Grossmann, *Farber-Zeit.*, 1915, **26**, 7; *J.*, 1916, 419.

[67] *Farber-Zeit.*, 1916, **27**, 134-137; *J.*, 1917, 59.

[68] *J. Soc. Dyers and Col.*, 1916, **32**, 244-245; *J.*, 1916, 1107.

[69] *J.*, 1916, 41.

[70] *J. Soc. Dyers and Col.*, 1916, **32**, 245-246; *J.*, 1916, 1107.

The industry of *re-dyeing* cannot yet boast of an extensive literature, but the industry has assumed large proportions and high scientific development in some countries. The methods adopted are principally matters of equipment, special methods being used for special purposes, and there is little desire on the part of the users of these methods to make them public property. C. M. Whittaker[73] shows that exposure to light and air affects the affinity of flannel for dyestuffs, and he suggests that the exposure results in the partial destruction of the amino-groups of the wool. M. Fort[74] states that the affinity of faded wool for various dyestuffs is erratic, basic colours being taken up more readily after the exposure, but acid colours show a less decided affinity. He suggests methods of treating the wool to overcome this erratic affinity. He further found[75] that wherever wool is browned by any agency, its affinity for dyestuffs is altered. Silk is similarly affected, but in a less degree. The browning of the fibre is said to be connected with the development or degradation of the amino-acids of the wool. Some interesting remarks on re-dyeing are also made by Lake.[76]

Slop padding is recommended in place of dyeing[77] on grounds of economy; by using an oil in the dyebath to assist the penetration, deep shades can be produced. Pack dyeing is discussed by F. Smith,[78] the difficulties, and methods of overcoming "channelling," being dealt with. In foam dyeing, P. Sisley[79] shows that the concentration

[71] Zanker und Weyrich, *Farber-Zeit.*, 1915, **26**, 337-341; *J.*, 1916, 687. See also Ahes, *J.*, 1910, 558, and *J.*, 1910, 672, 1915, 659.

[72] Act.-Ges. f. Anilinfabr., Ger. Pat., 293455, 1915; *J.*, 1916, 1153.

[73] *J. Soc. Dyers and Col.*, 1916, **32**, 4-9; *J.*, 1916, 41.

[74] *J. Soc. Dyers and Col.*, 1916, **32**, 109-111; *J.*, 1916, 534.

[75] *J. Soc. Dyers and Col.*, 1916, **32**, 184-187; *J.*, 1916, 833.

[76] *J. Phys. Chem.*, 1916, **20**, 761-808; *J.*, 1917, 133.

[77] G. Tagliani, *Farber-Zeit.*, 1915, **26**, 222-228; *J.*, 1916, 687.

[78] *J. Soc. Dyers and Col.*, 1916, **32**, 128-135; *J.*, 1916, 630.

[79] *Bull. Soc. Chim.*, 1917, **21**, 155-157; *J.*, 1917, 1127.

of colloids in a foam has a parallel in the concentration of colloids in the emulsified portion of an immiscible solvent, and the property of an emulsified liquid, *e.g.*, a "broken" soap bath, of dissolving much more than the normal amount of liquid is used to explain a number of dyeing processes involving the use of emulsions in fixing very slightly soluble dyestuffs. The use of silk-worm chrysalides instead of soap to produce the foam in foam dyeing has been protected.[80] Papers on wood dyeing[81] and paper yarn dyeing[82] have been published. The fastness of dyestuffs has been treated, and standards fixed by P. Heermann.[83] For testing the fastness of dyestuffs to light, A. Ganswindt[84] uses a lamp enclosed in marble plates, which have been soaked, at a high temperature and pressure, in a non-volatile hydrocarbon; although highly transparent, the marble absorbs the dark heat rays, and therefore provides a light eminently suitable for using in testing the fastness of colours to light. A method of determining alizarin in dyed fabrics is described by Leigh.[85]

A number of papers bearing on the theory of dyeing have appeared: it has been shown[86] that the adsorption of dyestuffs by colloidal clay increases with the colloidal nature of the dyestuffs, and that[87] amino-acids and polypeptides (and hence probably proteins such as wool and silk) combine with neutral salts to form molecular compounds during the dyeing process. Further, Fort has shown[88] that sulphuric acid employed in the dyebath combines with the wool base to form an additive salt which reacts by double decomposition with the salts of the colour acid of the dyestuff. Knecht and Hibbert,[89] in experimenting on the adsorption of dyestuffs by charcoal and silica, found that animal charcoal, in these experiments, could not be regarded as a form of the element carbon, since the nitrogen contents of the charcoal had a marked influence on its affinity for dyestuffs. This is an important observation, for one of the strongest supports of the mechanical theory of dyeing was the different behaviour of two forms of the same element, namely, graphite and animal charcoal, towards dyestuff solutions;

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[80] G. Schmid, Eng. Pat. 100336, 1915; *J.*, 1916, 630.
[81] Moll, *Z. angew. Chem.*, 1916, **29**, 405–409; *J.*, 1917, 132.
[82] Kertesz, *Chem.-Zeit.*, 1917, **41**, 43–44; *J.*, 1917, 287.
[83] *Mitt. K. Materialpruf.*, 1916, **34**, 153–156; *J.*, 1917, 590.
[84] *Farben-Zeit.* 1917, **53**, 49; *J.*, 1917, 960.
[85] *J. Soc. Dyers and Col.*, 1916, **32**, 205–213; *J.*, 1916, 888.
[86] Rohland, *Kolloid Zeits*, 1915, **16**, 16–18; *J.*, 1916, 685.
[87] Pfeiffer and Wittka, *Chem.-Zeit.*, 1916, 40, 258; *J.*, 1916, 597.
[88] *J. Soc. Dyers and Col.*, 1916, **32**, 33–40; *J.*, 1916, 304.
[89] *J. Soc. Dyers and Col.*, 1916, **30**, 226–230; *J.*, 1916, 1008.

it was shown[90] that the former behaved like cotton and the latter like wool in baths containing different dyestuffs. The relation between electrical endosmose and the adsorption theory of contact electrification has been shown[91]; the phenomena encountered in dyeing are said to be in accordance with the ionic adsorption theory. No further work has been done on the adsorption of dyestuffs and of moisture by textile fibres since it was shown[92] that an analogy exists between the adsorption by textile fibres of moisture from the air (*i.e.*, a vapour from a gaseous medium), and of dyestuffs from solution (*i.e.*, solids from a liquid medium). The question as to whether the absorption of moisture by vegetable fibres is a chemical or physical phenomenon is by no means settled, but the writer thinks that much enlightenment would result from further investigation of the two absorptions mentioned.

PRINTING

The use of resorcinol to dissolve the lakes formed by tannin with basic colours has been suggested[93]; it can also be used for discharging these colours on a tannin ground. For the fixation of acid dyestuffs on cotton, the use of the condensation products of aromatic amines and aldehydes has been protected.[94] Two methods of producing white and red impressions on indigo-dyed goods have been described,[95] and prints of great fastness to light are said to be produced by 1.4.5.8-tetrahydroxyanthraquinone, using an aluminium mordant.[96] The use of a reducing agent, a citrate, and "Blandola" (pure vegetable gelatin) for producing white or coloured reserves in printing with chrome colours has been patented,[97] as has also the use of phenol-formaldehyde condensation products for the fixation of metallic powders, pigments, or dyestuffs.[98] E. Dzieyk[99] describes the use of Manila copal and paraffin to produce by grinding with dyestuffs, dust-free, dry, transfer printing colours for embroidery work; the colours are fixed by spraying with alcohol. The production of novel effects in union fabrics by printing with substances which are capable of destroying one of the fibres present, then subjecting to a high temperature, has been protected.[100]

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[90] J. Hubner, *Chem. Soc. Trans.*, 1907, **91**, 1057, *J.*, 1907, 105-112.

[91] T. R. Briggs, H. L. Pierson, and H. S. Bennett, *Amer. Electrochem. Soc.*, May, 1917, *J.*, 1917, 1093.

[92] Higgins, *J.*, 1909, 188.

[93] Wosnessensky, *J. Soc. Dyers and Col.*, 1916, **32**, 278-280, *J.*, 1917, 80.

[94] Know Mill Printing Co., Ltd., and F. W. Weeks, Eng. Pat. 102291, 1916; *J.*, 1917, 80.

[95] G. Tagliani and Brosio, *Farber-Zeit.*, 1915, **26**, 1-3, *J.*, 1916, 419.

[96] Farbenfabr. vorm. F. Bayer und Co., Ger. Pat. 290075, 1914; *J.*, 1916, 598.

[97] Durand, Huguenin et Cie., Ger. Pat. 293359, 1915; *J.*, 1916, 1058.

[98] Bakelite G. m. b. H., Eng. Pat. 7284, 1916, *J.*, 1916, 734.

[99] Ger. Pat. 290598, 1914; *J.*, 19[illegible]6, 598.

MERCERISING.

A number of processes have recently been patented depending on the action of sulphuric acid of various strengths on cotton Mercer, in his original specification, mentioned the use of sulphuric acid of 105° Tw., but subsequent experience in mercerising showed caustic soda to be the best reagent to produce the swelling and lustreing of the fibre; moreover, it could be used without risk of damaging the material. Heberlein und Co.[101] produce novel effects on cotton fabrics by (1) alternately treating them with alkali lye of 15° B. and sulphuric acid of over 48° B., and (2) submitting the cotton fabric (previously mercerised) to the action, in places, of sulphuric acid of strength greater than 50·5° B, then washing and again mercerising.[102] Another method, devised for producing transparent effects on cotton, is by treatment with sulphuric acid of less than 50·5° B., cooled to at least 4° C., and subsequently mercerising with caustic soda.

A. Leighton[104] has investigated the absorption of caustic soda by cellulose and, after criticising previous work, supports Hubner and Teltscher's[105] conclusion that there is no experimental evidence of the formation of any chemical compound of cellulose with sodium hydroxide. Various explanations have been given of the fact that mercerised fibres absorb more moisture from the air and more dyestuff from solution than ordinary cotton fibres. R. Haller[106] states that the outer membrane of the cotton fibre consists of two structural elements, thus supporting Nageli's micellary-theory of the structure of vegetable membranes. The absorption of dyes and mordants by the penetration of those substances into the micellary interstices is dependent on the power of dispersion of the particles, and in the case of mercerised fibres, the micellae being more widely separated than in ordinary cotton, particles of larger size are admitted, thus accounting for the increased shade of dyeing produced.

No particular advance in the practice of mercerising can be recorded;

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[100] Zeidler, Ger Pat. 293400, 1914; *J*, 1916, 1057

[101] Eng Pat 100483, 1916; *J*, 1916, 1057.

[102] *J*, 1917, 133

[103] Akt.-Ges Cilander, Eng Pat 103432, 1916, *J*, 1917, 286

[104] *J Phys Chem*, 1916, **20**, 32-50; *J*, 1916, 249

[105] *J*, 1909, 641

[106] *Kolloid Zeits.*, 1917, **20**, 127-135; *J*, 1917, 923

in recent years attention has been devoted to the economy of the soda lye, and few changes in the process itself have taken place. Mercerised goods, hitherto imported from enemy countries in large quantities, have now been produced in this country, and there seems little possibility of this home trade being lost. The tests to distinguish mercerised from ordinary cotton, described by J. Hübner,[107] have been used with success in industry.[108] Of interest to mercerisers is a method of recovering lime from spent caustic mud by filtering and calcining in a kiln.[109]

FINISHING.

This branch of the industry has been little affected by the application of science, but in some branches there is evidence of the success of this application. The Austrians have made a success of the finishing of heavy mercerised goods, and they have done this by the special preparation of the cotton for this purpose; the spinning, weaving, and subsequent finishing have all been specially adapted to produce the best mercerised article, just as this special adaptation has been carried out in Germany to produce heavy "raised" cotton goods. Few papers on finishing have appeared. P. Bean[110] has discussed a number of modifications of starch, and the analysis of sizes and finishes has been treated by Lamb and Harvey.[111] Glue in place of starch has been suggested for sizing, and starch and diastafor in place of dextrin.[112]

The weighting of silk can be carried as high as 180%, according to Aumann,[113] the degree of weighting being influenced by the physical characteristics of the fibre. Heermann[114] states that no definite additive compound between the stannic chloride and the silk in weighted silk has been proved. He favours an electrolytic theory, the attraction of the silk being governed by the state of electrolytic dissociation of the stannic chloride.

The state of development of the industry and technical instruction in this branch of applied chemistry are dealt with at length in the writer's publication previously referred to.

Although the above is a short account of some of the important work which has recently been published, it must not be understood that the published work and patent specifications are a record of all the research work that is done in the industry. Publication offers few attractions to chemists engaged in the industry, because such work does not advance them in chemical circles, and is referred to as being of mere technical interest. Work known to have taken many years to accomplish, work scientifically carried out and admitted to be of high importance to the community, has been overlooked because it was said it made no direct contribution to science. Research students have, therefore, left technical problems alone, and in order to gain recognition, have turned their attention to investigations of purely scientific interest. This state of affairs, however, cannot be of use in assisting the application of science to industry.

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[107] *J.*, 1908, 105.

[108] Higgins, "Dyeing in Germany and America," 2nd ed., Longmans, Green and Co., 1916.

[109] J. H. Payne, *J. Ind. Eng. Chem.*, 1915, **7**, 1056-1059; *J.*, 1916, 111.

[110] *J. Text. Inst.*, 1915, **4**, 223-232; *J.*, 1916, 107.

[111] *J. Soc. Dyers and Col.*, 1917, **33**, 19-20; *J.*, 1917, 212.

[112] E. Ruf, *Z. ges. Textil Ind.*, 1915, **18**, 140; *J.*, 1916, 419.

[113] *Farber-Zeit.*, 1915, **26**, 301-303; *J.*, 1916, 630.

[114] *Mitt. k. Materialpruf.*, 1915, **33**, 446-453.

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ACIDS, ALKALIS, SALTS, &c.

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The period covered by this second report is naturally still strongly influenced by the continued activities arising from military needs. The effects of the restricted supplies of some raw materials have been severely felt in certain directions, and the efforts made to apply substitutes have in a large number of cases been successful.

A paper read before the American Chem. Soc., in April, 1916, gives an account of the influence of the war on American chemical industry. The cessation of shipments of potash salts from Germany, and the almost total stoppage of the importation of dye-stuffs, have been seriously felt. Great activity has been shown in assisting to meet this acute situation. The growth of the soda industry is indicated by the census of manufactures. In 1914, 1,371,105 metric tons of soda products were manufactured, being an increase of nearly 42% over that of 1909. The consumption of pyrites in the United States in 1915 reached a new high level, 1,358,768 tons, due chiefly to the unprecedented demand for sulphuric acid. The domestic production was 394,124 long tons, an increase of 57,162 tons over that of 1914.[1] The exports of sulphur fell from 98,163 tons in 1914 to 37,312 tons in 1915. Sulphuric acid supplies have been inadequate since the middle of 1915.

The following production figures from the U. S. Geological Survey, 1916, are of interest:—50°B. acid, 1,518,271 metric tons; 60°B., 657,976; 66°B., 1,019,024; oleum, 189,795; total reduced to 50°B., 3,868,152, of which smelters contributed 1,056,830.

The war has compelled Russia to develop her own chemical industry, and the progress has been fairly good in spite of the hindrance caused by the great shortage of materials and machinery. The supply of Russian pyrites is increasing, new deposits have been found near the railway at Kinel in the Boguruslav district, and sulphur is reported near Samara. New vitriol works have been erected in the Volga region, in the Donetz basin, in the Caucasus, and in the Urals. The Ekaterinburg works produced 1,700,000 poods (28,000 tons). The factory at Kishtyn was destroyed by fire, but an attempt was made to resume in 1917.

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[1] 1916, 1107.

The chemical and allied trades in Japan have been affected by the industrial changes to a degree approached by few other branches of manufacture. The annual production of about 300 tons of chlorate of potash has increased to over 3,500 tons. Factories for the manufacture of soda ash and bleaching powder, zinc refineries, glass works, &c., have been erected. These examples indicate that her influence as an industrial nation on the markets of the world is increasing rapidly.

The Government returns for 1915[2] give the following figures:—sulphuric acid, 1,170,000 lb.; hydrochloric acid, 1,819,000 lb.; caustic soda, 249,000 lb.; and acetic acid, 723,260 lb.

The progress made by the chemical industry in France since the outbreak of war has been such as to make her henceforth practically independent of Germany for the majority of products formerly obtained from that source. Idle works, largely at the instance of the Ministry of Commerce, have again been set in operation, and the future of the industry secured. The output of oleum, of which 75% was formerly imported, is now in one single Department equal to one-half of the total pre-war consumption. The Magnésie Française has discovered an improved process for the manufacture of sulphuric acid by means of magnesium salts. Very substantial development has been made in the production of nitric and hydrochloric acids, also liquid chlorine and bromine.

For some years before the war, Germany imported 900,000 tons of pyrites from Spain, and 100,000 from Norway. The home production was about 300,000 tons, mainly from Megen in Silesia. In 1912/13 the importations from Spain amounted to 1,200,000 tons. The production of sulphur trioxide from gypsum[3] may have been accomplished in an electric furnace, or by the reaction with silica at a high temperature.

It is no exaggeration to say that the part played by the chemical industries in assisting the allied nations to carry on the war has grown in greater proportion with the reconstruction of industry generally. In 1916 the imports of chemicals to the United Kingdom were valued at £28,663,150, an increase of about £9,319,150 over those of the previous year. Exports were valued at £27,676,810. The pyrites production is given as 10,535 tons for 1915. The number of works registered under the Alkali Acts is 1372 in 1915 (1356 in 1914), of which 63 were alkali works.

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[2] *Chem. Trade J.*, 1916, **59**, 7.

[3] *Chem. Trade J.*, 1917, **60**, 188.

SULPHURIC ACID.

A considerable number of modified vitriol plants have been erected and many of these are now in operation. There is little doubt that for all strengths above 140°Tw. the unmodified chamber system will be supplanted by other types, but for the lower strengths the smaller initial outlay will count in favour of its continuance. The working of tower systems demands an amount of skilled chemical control which has so far seldom been afforded to the chamber systems. The omission of scientific control has frequently so severely handicapped the older systems that results have not been of the highest possible order. The chief advantage of the chamber plant is the elasticity due to the fairly wide margins of working conditions, and it is probable, on this account, that installations in the future will be a combination of a tower system with chambers, the latter to give the elasticity previously mentioned. The proposal has been made to assist existing plant, both tower and chamber, by introducing contact units to enlarge the capacity of the system without increasing the number of chambers, and there seems to be much promise in such reinforced methods. The writer is of the opinion that the introduction of methods of utilising nitrogen from the air or the oxidation of ammonia to produce the nitrous gases, will be an important feature of sulphuric acid manufacture in the near future. The increased use of the Cottrell precipitator,[4] and the employment of concentrators of the Gilchrist type[5] are likely to exert a far-reaching influence throughout the chemical industry.

An interesting method of producing sulphuric acid by the electrolytic oxidation of sulphur dioxide is described by Thompson.[6] A nickel cathode in an earthenware cup, which acts as diaphragm, containing sulphuric acid or sodium sulphite, is employed. The anode of platinum gauze is immersed in a solution of sulphur dioxide kept at 1–5% strength. A current density of 0·0075 amp per sq. cm. causes a ready oxidation to sulphuric acid up to 95% oxidation with a high current efficiency even in strong solutions. For a given concentration of sulphuric acid, the current efficiency decreases with increasing current density. Waggaman's suggestion[7] was referred to last year (Vol. I., 111), and attention is drawn to the temperature control by water cooling the sinuous tunnel conveying the Glover tower gases to the first chamber. A cylindrical chamber is described by Harris and Thomas[8] Arrangements are made for directing sprays of weak acid or water on to an interior wall or curtain, and on to a central column, extending nearly to the roof of the chamber, which forms the outlet for the exit gases. The inlet pipe is set tangentially. The temperature is readily controlled. In the last chamber the central column may be packed and thus caused to replace to some extent the absorption towers at the end of the system. Oliver[9] achieves temperature control of the chambers by surrounding them with housings which form special air cavities through which natural or forced draught circulates. The use of nitrating towers (12 × 4ft.) down which a nitre solution is caused to flow has been patented by Macadam and Walker.[10] The Curtius (Duisburg) system (Vol. I., 110) is again referred to here with fuller detail. The arrangement of the towers is given in the accompanying diagram:

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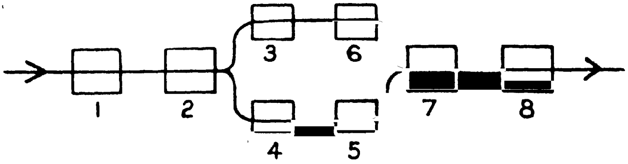
[4] *Jour. Ind. Eng Chem.*, 1911, **3**, 542; 1917, **9**, 26, *J*, 1911, 1037, 1916, 1154; **1917**, 134; *C.T.J.*, 1917, **60**, 6.

[5] Eng Pat. 105,993, *J.*, 1916, 1015.

[6] *Met. and Chem. Eng.*, 1916, **15**, 677; *J.*, 1917, 81.

[7] *U.S. Dept. Agric.*, Bull. 283, and U.S. Pat. 1,185,029 (1916); *J.*, 1916, **42 and 736**.



Alternative methods of working are as follows:—

(A.) No 8 is sprayed with Glover acid, and the product, with the acid from other towers, is taken to No. 1, where it is de-nitrated. Some of the de-nitrated acid is removed and conveyed to No. 8 Acid flows between Nos. 2 and 7, 3 and 6, 4 and 5, in both directions.

(B.) No. 8 receives the Glover acid, and the product passes to Nos. 7, 2, and 1, in succession, the acid from the other towers also to No. 1, where de-nitration takes place. Towers 3 and 6, and 4 and 5, work in a closed circuit.

The recovery of acid in the Gay-Lussac exit gases by washing with water, which may then be used for sprays in the chambers, is the subject of Laufer's patent.[11] The manufacture of vitriol from smelter gas has attained enormous proportions in the United States. The Montana, the Anaconda, and the Garfield Cos. use gas from McDougall furnaces roasting sulphide fines. The Tenessee and the Ducktown Cos.

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[8] Eng. Pats. 104,461 (1916) and 6026 (1915); *J*, 1917, 502.

[9] U.S. Pat. 1,229,316 (1917); *J.*, 1917, 872

[10] Eng. Pat. 103,877 (1916); *J.*, 1917, 385.

[11] Fr. Pat. 481,131 (1916); *J*, 1917, 136.

utilise gas from blast furnaces in which pyritic smelting of ores carrying 30% of pyrrhotite, 6% of pyrite, and 8% of chalcopyrite with the addition of 4·6% of coke is carried out. The resulting gas is normally: Sulphur dioxide 8·9%, carbon dioxide 6·7%, carbon monoxide 0·8–1%, and nitrogen 84%; air is admitted at several points to avoid undue dilution of the sulphur dioxide. The nitre consumption is about 6·8%. Owing to impurities in the gases the chamber process is used.

The recovery and concentration of vitriol is the subject embodied in a number of patents published during the year. In one taken out by the Armour Fertiliser Works,[13] acid is caused to trickle down an irregular inclined surface so as to form pools and films, in an enclosed chamber and exposed to hot gases at the lower part. The hot gases are directed towards the surface of the acid by baffles. Oliver[14] describes a concentrator which is likely to prove a highly efficient form of apparatus, better known perhaps as the "Gilchrist" concentrator. Hot gases pass over the surface of the acid and then upwards through a tower down which acid is also flowing. The acid is agitated by air jets. The main object of the invention of Dreyfus[15] is to obtain a high percentage acid with simple apparatus of cast iron. Sulphuric acid of about 92% is further concentrated in a vessel consisting of an outer cylindrical cast iron pan fitted with a lid, and containing a series of concentric cylinders alternately supported by the pan and lid. The acid is fed into the innermost space and passes alternately down and up to the outermost space, which it leaves by an overflow pipe. Advantage is taken of the facts (*a*) that a 90–93% acid does not attack cast iron, (*b*) that in the concentration of vitriol the higher strengths are at the bottom, (*c*) that water is eliminated gradually, (*d*) that this gradual elimination is effected by extensive travel through many vessels. The Duron[16] method consists in passing hot gases through horizontal flues above a series of parallel channels containing the acid to be concentrated and then over the acid in the reverse direction. The re-heating of the gases, by contact with the hot flue above, is greatest at the exit. The arrangement affords the largest surface of evaporation with the minimum speed of flow and the greatest volume of hot gases at the point where the acid is weakest. With four channels concentration from 65–67% up to 98·3% was

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[12] *Eng. and Min. J.*, 1916, **102**, 1121; *J.*, 1917, 133.

[13] U.S. Pat. 1,183,207 (1916); *J.*, 1916, 736.

[14] Eng. Pat. 105,993 (1917); U.S. Pat. 1,195,075 (1916); *J.*, 1916, 1015.

[15] Eng. Pat. 101,642 (1916); *J.*, 1916, 1155.

[16] Eng. Pat. 104,034 (1916); *J.*, 1917, 385.

achieved. Kilroy[17] proposes to concentrate vitriol in a series of towers, packed with refractory material and provided with a lead pan at the bottom. The acid is sprayed into the hot gases. The working principle of Skoglund's[18] apparatus is similar, the hot gases being caused to pass through a spray of acid. The weak acid is passed into one end of a container fitted with an arrangement for spraying by means of a suitable gas under pressure, and the strong acid is drawn off at the other end of the vessel. Another form of concentrator,[19] of rather complicated design, is best described as a vertical cascade. It consists of super-imposed circular units each containing a shell, funnel, annular ring, and guard, the whole surrounded by the heating space.

The Soc. Anon. Fabr. de Soie Artificielle[20] describe a multiple-effect design of plant for vitriol concentration. The original patent must be consulted for the details. The invention relates to the use of elements so arranged as to utilise as completely as possible the heat contained in the vapour produced, with the least possible disengagement of the sulphuric acid. The idea is ingenious and might find use in certain cases, but the complexity of the apparatus must militate very strongly against its adoption in the majority of cases.

A series of interesting details of the working of a tower plant for the production of 93–97 % vitriol is given by Armstrong.[21] In practice, a tower packed with quartz, with an oil flame as the source of heat, required washing after ten days' working. The quartz was found to have disintegrated considerably and only 63° B. acid was produced, probably owing to the openness of the packing. Small quartz was added to make up for the shrinkage and loss, amounting in several months to the original quantity of packing. When working well, a temperature of 1200–1400° F. (650°–760° C.) for the entering gas and 280°–290° F. (138°–143° C.) for the exit gas was recorded, the suction being [illegible] inch at the top. Should the exit temperature fall to 250° F. very little 66° B. acid is produced; to remedy this the tower is cooled by weak acid and washed with water for twelve hours. When the top temperature is too high (350–360° F.) owing to the packing being too open, the suction at the top will be very small. The brick lining is cemented with silicate and "silax" cement. With 60,000 lb. of 60° B. acid per 24 hours, the loss would be 2000–4000 lb. of 60° B. and 39,000 lb. 66° B. produced; the balance of 9200 lb. 60 B. is recovered in the scrubbers as 46° B. acid. The loss varies with the draught, being smallest when there is just enough pull to take the distillate from the towers.

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[17] U.S. Pat. 1,211,594 (1917); *J.*, 1917, 214.

[18] U.S. Pat. 1,232,109 (1917); *J.*, 1917, 925.

[19] *C.T.J.*, 1917, **60**, 90.

[20] Eng. Pat. 10,386 (1915); *J.*, 1916, **537**.

[21] *J. Ind. Chem. Eng.*, 1917, **9**, 386; *J.*, 1917, 501.

Blowske[22] suggests recovering the waste acid from petroleum refining by diluting to free from tarry matter, followed by rapid distillation to minimise reduction by the organic matter

The production of vitriol combined with the manufacture of cement is suggested by Basset.[23] A mixture of clay and material containing gypsum is heated sufficiently to form cement and gases containing sulphur dioxide The gaseous products mixed with air are passed over a catalyst of natural hydrated oxide of iron mixed with gypsum. The sulphur trioxide is removed and any unconverted dioxide absorbed in calcareous material suitable for use in the production of cement. Dirks[24] proposes to produce ammonium sulphate by the action of ammonia and carbon dioxide on gypsum or anhydrite, by treatment with phosphoric acid, sulphuric acid free from arsenic and selenium is obtained The residual ammonium phosphate on heating is converted into phosphoric acid and ammonia, which are thus recovered

The use of several catalytic agents has been claimed during the past year. The Ellis Foster Co.[25] suggest as catalysts (*a*) active voluminous chromium oxide and an oxy compound of an easily fusible heavy metal which is capable of absorbing sulphur dioxide, acting also as a binding material for the chromium oxide without combining with it.; (*b*) voluminous chromium oxide and tin oxide, one being in excess of the amount necessary to form tin chromate A later patent[26] supplements the former Gases containing sulphur dioxide and oxygen are passed over tin chromate at the catalysing temperature. The sulphur trioxide is absorbed and the remaining gases again passed over the chromate. The catalyst must be free from fixed alkalis. Fahrenwald[27] suggests compounds of silver and vanadium in the place of platinum as a contact substance Palladium with silver, gold, tungsten, or molybdenum are also mentioned, alloys of the last two elements with the precious metals are even more efficient than platinum and its alloys. Kee and Wedge[28] propose to assist the chamber process by exposing the gases from the Glover towers or at other points between the Glover and Gay-Lussac towers to an electric discharge.

The question of the chamber process control has been treated at

[22] U.S. Pat 1,186,373 (1916), *J.*, 1916, 839.
[23] U S. Pat 1,197,331 (1916); *J*. 1916, 1058
[24] Ger Pat. 295,906 (1915), *J*, 1917, 646.
[25] U S Pats. 1,204,141/2/3; *J.*, 1916, 1260.
[26] U.S. Pat. 1,227,044 (1917), *J*, 1917, 711
[27] ***Bull. Amer. Inst. Min. Eng***; *J.*, 1917, 81.
[28] U.S. Pat. 1,220,752 (1917); *J*, 1917, 547.

some length by Fairlie.[29] His main conclusions may be summarised as follows:—With 9–10 % of oxygen in the burner gases, 6½–7½ % of sulphur dioxide should yield a 5 % exit. Determinations of the total acids leaving the Glover tower are useful. The temperatures should be noted at the front and back of the first chamber, and gauges should be furnished to show the speed of the gases. "Drips" should be compared with the bottom acid and both acids should be tested for strength and nitre content. The acid circulation must be maintained by chute arrangements. The amount of sulphur dioxide leaving the last chamber should be 0·1–0·2 % and the oxygen 5 % or more. Gay-Lussac temperatures to be 90–100° F., the acid 140° Tw., the nitre should be estimated thrice daily, and exit tests should show 1·8–2 grains. A fan, between the absorbing towers, making 300–400 revs., is recommended. With reduced chamber space the nitre in circulation must be raised, and this increases the wear and tear of the plant.

The determination by Ditz and Kanhauser[30] of the solubility of lead sulphate in concentrated sulphuric acid is of interest. The solubility increases slowly with the concentration up to 97% H_2SO_4, then rapidly to 100%. From the maximum at 100% the curve falls to about 5% trioxide, rises rapidly to 15% and less rapidly to 22% free sulphur trioxide.

A reference to the sampling of oleum[31] is of interest and bears out the experience of many works chemists. When one litre of oleum was left exposed for three hours in an 8 cm. dish, the surface sample gave 6 % of free trioxide, the middle 28%, the bottom 30 %, and after agitation 34·5, 36·5, 37·5, and 36 %. It is of the greatest importance to render the oleum homogeneous, a current of dry air being a satisfactory means of doing this. A point frequently neglected in connection with the conveyance of materials in tank waggons is the colour of the paint. An observer[32] has noted the rise of temperature under similar conditions of benzene tanks, variously coloured, with the following results:—Black 54°, light grey 26·3°, white 22·5°, aluminium paint 20·5°, tin paint 19·8°.

The utilisation of nitre cake has been the subject matter of several communications to the technical journals. Grossmann[33] describes the steps by which caustic soda may be produced (cp. Vol. I., 111).

(1.) $3Na_2SO_4 + H_2SO_4 + 2CaSO_3 = 2NaHSO_3 + 2CaSO_4 + 2Na_2SO_4$;

after the removal of the calcium sulphate, lime is added.

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[29] *J.*, 1917, 196 and 491.

[30] *Z. anorg. Chem.*, 1916, **98**, 128; *J.*, 1917, 641.

[31] *C.T.J.*, 1916, **59**, 417.

[32] *C.T.J.*, 1917, **60**, 365.

[33] Eng. Pat. 12,832 (1915) *J.*, 1916, 1059.

$$(2.)\ 2NaHSO_3 + 2Na_2SO_4 + Ca(OH)_2 = Na_2SO_3 + CaSO_3 + 2Na_2SO_4 + 2H_2O.$$

The calcium sulphite is removed and more lime added

$$(3.)\ Na_2SO_3 + CaSO_3 + 2Na_2SO_4 + 2H_2O + Ca(OH)_2 = 2NaOH + 2CaSO_3 + 2Na_2SO_4 + 2H_2O;$$

(2) and (3) may be combined, and heating or augmented pressure may be used. The calcium sulphite is removed, washed, and used again. The caustic liquor is evaporated until the sodium sulphate crystallises out; after separation of this, further evaporation is necessary. Kerr[34] proposes to heat a mixture of two mols. of nitre cake with one mol. of magnesium chloride and a little water; hydrochloric acid is evolved and a mixture of soda and magnesium sulphate results. According to Llewellyn and Spence[35] nitre cake and a reducing agent such as 25% iron pyrites are caused to react in a closed agitator. Sulphur and sulphur dioxide are evolved, sodium sulphate and iron oxide remaining; by employing metallic iron instead of the sulphide no free sulphur is produced and a steady stream of dioxide is obtained.

Grossmann[36] suggests further interesting possibilities of working up nitre cake. He finds that under certain conditions nitre cake, sodium nitrate, and carbon react practically quantitatively to produce, without frothing, nitrous gases at comparatively low temperatures. The ingredients must be finely ground and intimately mixed, the carbon being in slight excess and a current of air passed. The gases might be passed directly to the chambers or towers instead of condensing them. The residue could be utilised in the Leblanc revolver for caustic soda. The carbon may be omitted. The grinding of nitre cake can be greatly facilitated by pouring the fused cake on to a thin layer of soda ash, and chilling, thus producing a spongy and friable mass. The soda ash may be mixed with sulphate and by so doing about 2½% is sufficient. Other long papers dealing largely with this subject have appeared, notably that of Brownsdon suggesting its use as a pickle for annealed brass with recommendations for working,[37] and of Kilburn Scott[38] on the economy of acids in the metal trades. Further notes and experiences were contributed recently at the meeting of the Nottingham Section.[39]

There are certain valid objections to the use of nitre cake in bleaching cotton fabrics, especially those required for printing.[40] It cannot be used for alizarin as the lime boil is indispensable, and probably not for light shades with direct and basic colours. There is undoubtedly much undue conservatism amongst possible users of nitre cake, which doubtless hinders its more extended use, as does the non-employment of chemically trained men in many branches of manufacture

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[34] U.S. Pat. 1,203,357 (1916); *J.*, 1916, 1260.

[35] Eng. Pat. 103,689 (1916); *J.*, 1917, 385.

[36] *J.*, 1917, 1035.

[37] *J.*, 1917, 575.

[38] *J.*, 1917, 812.

[39] *J.*, 1917, 1216A.

[40] *C.T.J.*, 1916, **59**, 392.

HYDROCHLORIC ACID.

The manufacture of hydrochloric acid, by spraying a fused alkali chloride with sulphuric acid, or a mixture of this with air or steam, or sulphur dioxide and steam, is the object of a patent of the Salzwerk Heilbronn.[41] Hydrochloric acid is liberated and the sulphate left as a fine powder Clayton and Metals Research Co [42] achieve the direct combination of hydrogen and chlorine by heating the moist gases, in the ratio of 10 : 7 to a temperature not below 340° C. in the presence of wood charcoal

NITRIC ACID

The enormous growth of the newer methods in the nitric acid industry may be gathered from the following statistics At the end of 1915 there were thirty installations of the Frank-Caro system producing about 400,000 tons per month; Pauling's modification of the Birkeland-Eyde plant at Muhlenstein producing 6000 tons per annum; and about 300,000 tons of ammonium sulphate was made by the Haber process. The Royal Waterfalls Board report the utilisation of 12,000 kw. to produce 7000 tons of nitric acid and nitrates at Trolhattan by the Birkeland-Eyde plant: also a production of 6000 tons of carbide by the Kvina Carbide Co, by means of power from the Troelands waterfall.

The sodium nitrate production for the year ending June 30th, 1917, was 70% in excess of that for the preceding year, but still below the pre-war figures.[43] A full account of the nitrate industry in Chili is given by Hobsbaum and Grigioni.[44] The synthetic production of nitric acid has been the subject of several articles of considerable length to which the reader is referred. Attention may be called especially to that of Kilburn Scott, which is accompanied by many diagrams of types of arc furnaces,[45] and that of Maxted on the synthesis of ammonia and its oxidation to nitric acid.[46] An attempt to compare costs of the catalytic oxidation of ammonia with those of the arc process and from sodium nitrate is furnished by Zeisberg,[47] but the figures must be regarded with reserve. It is concluded that the catalytic methods cannot compete with the other processes. On equal yields of 97% nitric acid, the Ostwald would have, from the figures given, the advantage of about one farthing over the nitrate method, but according to the most trustworthy evidence, the conversion efficiency of the Ostwald process appears not to exceed 85%. The electric resistance of mixtures of oxygen and nitrogen may be diminished by addition of steam.[48] The oxides of nitrogen, to prevent dissociation, are cooled and passed on to a vessel containing sulphuric acid and water, air also being introduced. The direct use of nitrogen oxides from the Frank-Caro process is not recommended owing to practical difficulties. Petersen[49] describes a condenser plant of nine "Putzen" touries, followed by three towers for the main condensers, as the most economical yet devised. The gain in cost for 1200 kilos. nitric acid (1.33 sp. gr.) per 24 hours is given as 0.6 mark per 100 kilos.

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[41] Ger. Pat 295,074 (1915); *J.*, 1917, 503.

[42] U.S. Pat. 1,220,411 (1917); *J.*, 1917, 547.

[43] *J.*, 1916, 1058.

[44] *J.*, 1917, 52.

[45] *J.*, 1917, 771.

[46] *J.*, 1917, 777.

[47] *Met. and Chem. Eng.*, 1916, **15**, 299; *J.*, 1916, 1107.

A series of five related patents by the Norsk Hydro Elektrisk Kvaelstofaktieselskab illustrate some of the difficult points in the working of the plant.[50] According to one patent, nitrogen compounds are produced by arc oxidation, which, as well as the absorption of the products, is effected in a closed system; finally a gas rich in argon is obtained. The accumulation of impurities is avoided by the withdrawal of a portion from time to time. Another process avoids the necessity of an air-tight system by working under a diminished pressure, and compensating for leakage by the withdrawal of a portion after absorption. For plus pressures the system previously mentioned is used.

Solutions of ammonium nitrate act as absorbers for both ammonia and nitrous gases[51]; separate portions of the solution are saturated with each gas and then mixed to obtain a stronger neutral solution. By repeating the process concentrated solutions or crystals are finally obtained. By dissolving a metal, capable of forming a nitrate, in dilute nitric acid and decomposing the salt with steam, oxides of nitrogen are produced; with the addition of air to form peroxide, nitric acid is obtained.[52]

The employment of sulphuric acid as the absorbing agent is also suggested.[53] The denitration of the concentrated acid containing the nitrous gases is effected in a tower containing acid-resisting material, up which the vapour of 60% nitric acid and air is passing. By condensing the exit gases fuming nitric acid is obtained, which may be decolorised by blowing with air. The sulphuric acid of about 80% strength requires little concentration for further use as absorbing liquid for nitrous gases.

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[48] Rankin. Fr. Pat. 479,492 (1915); *J.*, 1916, 1108. U.S. Pat. 1,150,786 (1915); *J.*, 1915, 960.

[49] *Met. und Erz*, 1916, 197; *Chem.-Zeit.*, 1917, **41**, *Rep.*, 70; *J.*, 1917, 641.

[50] Fr. Pat. 480,205 (1915); *J.*, 1917, 215. Eng. Pat. 100,099 (1916); *J.*, 1917, 214.

[51] Eng. Pat. 101,090 (1916); *J.*, 1917, 1007.

[52] U.S. Pat. 1,236,662 (1917); *J.*, 1917, 1047.

[53] U.S. Pat. 1,197,295 (1916); *J.*, 1916, 1260.

The Nemours Powder Co.[54] has also patented a similar method. The nitric acid and a dehydrating agent, such as sulphuric acid, pass continuously into a chamber from which nitric acid is driven off by steam from a boiling solution of the dehydrating agent, or from weak nitric acid previously concentrated by the process. The diluted sulphuric acid is removed continuously, the nitric acid condensed, and any oxides of nitrogen absorbed in water. The Stolberg Works[55] employ the oxidation of ammonia (Frank-Caro) in their vitriol chambers to replace nitre. The ammonia is generated from 25% liquor by distillation with lime, followed by purification by caustic soda from sulphuretted hydrogen, phenol, &c. The vapour is passed over platinum gauze heated to 700 C. by 125–150 amps. at 20–25 volts. The nitrous gases are introduced into the tunnel between the Glover tower and the first chamber or direct into the first chamber. Flap valves are provided to prevent the poisoning of the platinum in case the fans stop. It is likely that a device of British origin to accomplish the same intention will be in use in a short time.

The Badische Co. have taken out a number of patents relating to the use of a variety of catalytic masses.[56] The bismuth or bismuth oxide may be replaced by tellurium or a tellurium compound in an amount which may be varied within wide limits, and upon a carrier of a noble metal or an indifferent substance The following may be used as contact masses at 700°–800° C.: (1) Powdered firebrick soaked in 10–20% solution of platinic chloride and in a solution of about 10% ammonium or sodium tellurite (either separate or mixed); (2) a metal of the platinum group is deposited on a carrier and then rendered active with a small amount of tellurium or tellurium compound; (3) granular cupric oxide is soaked in a 5% solution of ammonium tellurite and dried.

A method of temperature control is described in a patent of the Ellis-Foster Co.[57] The hot mixture of ammonia and air is passed upwards through a coarse mass of catalyst, cooled by a mixture of air and ammonia in an embedded conduit. The spent catalyst can be withdrawn at the bottom of the chamber.

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[54] U.S. Pat. 1,197,167 (1916); *J.*, 1916, 1058.

[55] *Met. und Erz*, 1916, Jan. 22; *C.T.J.*, 1916, 59.

[56] Eng. Pats. 7651, 13,297, 13,298, 13,299 (1915), 13,848 (1914); *J.*, 1916, 1008 and 1015.

[57] U.S. Pat. 1,233,564 (1917); *J*, 1917, 1007.

A similar catalyst, platinum free from iridium, with controlled electrical heating, has been patented by Landis.[58] Washburn[59] passes a mixture of oxygen and ammonia over the catalyst at such a speed that the product contains nitrous gas and not more than 20% of ammonia, thus producing a mixture of nitric acid and ammonium nitrate. By the addition of a further quantity of ammonia, ammonium nitrate is produced. Anderson[60] discusses the oxidation of ammonia according to the equation $4NH_3 + 7O_2 = 4NO_2 + 6H_2O$. The velocity of this reaction is increased by suitable catalysts. The progress of the reaction is determined by the equilibrium expressed by $4NH_3 + 5O_2 = 4NO + 6H_2O$. This is exothermic, hence the higher the temperature the more ammonia remains unchanged when equilibrium is established. In the presence of excess of oxygen oxidation is practically quantitative within a large temperature range. A mixture of air with 2·5–5% of ammonia at 500–1000° (absolute), passed at such a speed that contact is assured for 0·18–1·15 second, is converted to the extent of 95%. Any catalyst favourable to the reaction $N_2 + O_2 = 2NO$ is unsuited for ammonia synthesis.

Ellis[61] employs silver molybdate as an oxidising catalyst of ammonia. An account of the processes for the fixation of nitrogen and the application of these to the manufacture of a variety of chemical substances and other industrial uses is given by Bucher.[62]

AMMONIA.

The production of ammonia from Mond gas is suggested by Perry,[63] by passing the gas, or a mixture with steam, through iron pipes or through a furnace of iron or refractory containing coke or carbonaceous material at a temperature of 650°–700° C. The ammonia is removed by sulphuric acid and the gas treated again.

The combination of nitrogen and hydrogen under pressure to form ammonia was discovered by Chatelier[64] in 1901,[65] but owing to an explosion the method was abandoned. The process was brought to a successful issue by Haber in 1908.

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[58] U.S. Pat. 1,193,796/1,193,800; *J.*, 1916, 963.

[59] U.S. Pat. 1,217,247 (1917); *J.*, 1917, 503.

[60] *Zeit. Elektrochem.* 1916, **22**, 441; *J.*, 1917, 81.

[61] U.S. Pat. 1,237,884 (1917); *J.*, 1917, 1094.

[62] *Amer. Inst. Chem. Eng.*, Jan., 1917; *Jour. Ind. Eng. Chem.*, 1917, **9**, 233; *J.*, 1917, 451.

[63] Eng. Pat. 103,118 (1916); *J.*, 1917, 215.

[64] *Comptes Rend.*, 1917, **164**, 688; *J.*, 1917, 545.

[65] Fr. Pat. 313,950 (1901).

Ellis[66] brings about the union of hydrogen and nitrogen by means of coconut charcoal carrying cerium and a small quantity of another base such as lanthanum, didymium, or yttrium, capable of increasing the activity. Classen[67] combines the employment of both silent and spark discharges, in addition to a catalyst. Metals and alloys supported on acidic carriers, are mentioned, silica from water-glass being especially suitable as it adsorbs colloidal metals such as gold, platinum, etc. The mixed gases are passed over a suitable catalyst between electrodes, one of which is a good conductor such as copper, the other a bad conductor such as glass or porcelain. The latter may be immersed in water and may concentrically surround the former, with the contact material between. The temperature may be 25°-90° C and pressure normal or above normal A cyclic process is described by Thorsell[68] The residual barium formate produced in the decomposition of barium cyanide is treated with sodium carbonate to form barium carbonate and sodium formate The solution is evaporated *in vacuo* to obtain the salt which is ultimately converted into sodium oxalate The barium carbonate is heated with coal and nitrogen to reproduce barium cyanide. The combination of hydrogen, nitrogen, and chlorine under the influence of a silent discharge is claimed by Mayer[69] Water or steam is injected to prevent reversal and to remove the products

The use of magnesium sulphate in the production of ammonium sulphate is suggested by Precht.[70] By treatment of the magnesium salt with excess of ammonia, preferably under pressure, a double sulphate is produced which crystallises first on concentration, leaving nearly pure ammonium sulphate in solution. The double salt on further treatment with ammonia yields ammonium sulphate and magnesia. The production of ammonium sulphate from the sulphite is achieved, according to a patent of the Elektrizitatswerk Lonza,[71] by using calcium sulphate as an oxygen carrier. The calcium sulphite which is first formed is more readily oxidised than ammonium sulphite. The purification and neutralisation of ammonium sulphate is brought about by Capron[72] by washing with a saturated neutral or alkaline solution of ammonia sulphate and "jigging." Ammonium bicarbonate and sodium nitrate may be caused to react at 50° C. under pressure in the presence of a small amount of water. Ricard[73] treats the mixed dry salt with hot water so as to dissolve the ammonium nitrate, which after refining is again washed with cold water to remove the sodium nitrate remaining in the product. Huhn[74] causes an aqueous solution of calcium nitrate (from the arc process) to react with ammonium sulphate at a temperature of 120° C. or higher. A discussion as to the relative merits of direct or indirect methods of ammonia recovery in coke-oven practice is contributed by Riley.[75] The "indirect" method is stated to possess many disadvantages and no advantages. The semi-direct system of Koppers does not give rise to naphthalene troubles, the risk of ammonia losses is lessened, the effluent reduced in quantity owing to the smaller steam consumption, the sulphate is of better quality, and the process is simpler and more efficient. The "direct" method requires more power, involving more wear and tear, and produces a thicker and more troublesome tar.

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[66] U S. Pat 1,184,839 (1916); *J*, 1916, 737.
[67] Eng Pat 14,055 (1915), *J* 1917 547
[68] Eng Pat. 292,218 (1915), *J*, 1916, 963
[69] Fr Pat 480,232 (1915); *J*, 1917, 137
[70] Ger. Pat. 292,218 (1915); *J*, 1916, 839.
[71] Eng. Pat. 105,906 (1917); *J*., 1917, 1093.
[72] Eng. Pat. 108,990 (1916); *J*, 1917, 1093.

HYDROGEN

An article by Baritz[76] contains a full summary of the Messerschmitt process and a comparison with other processes for the production of hydrogen. Reference may be made here to two patents of interest in the technical production of this gas. Maxted and Ridsdale[77] draw attention to the fact that hydrogen produced by passing steam over iron prepared from its oxide by reduction in water-gas or other commercial reducing gas, contains a considerable quantity of carbon monoxide. To obtain hydrogen free from this contamination, a gas containing substantially more carbon dioxide than monoxide is used to reduce the oxide of iron. Dilution of the gas by nitrogen must be avoided. The carbon dioxide prevents the otherwise unavoidable deposit of carbon during the reduction, and therefore there is no carbon monoxide in the hydrogen produced by passing the steam over the heated iron. The Badische Co.[78] maintain that contact masses of pumice saturated with solutions of nickel or cobalt chlorides are not suitable for the reaction $CO + H_2O = CO_2 + H_2$, good yields however are afforded by using relatively small quantities of solutions of nickel salts free from halogens and sulphur. The method of producing hydrogen by the decomposition of water under pressure is of interest.[79] Experimental apparatus was filled with iron powder, water, and some electrolyte. By heating, hydrogen was produced under 300 atmos. pressure, thus avoiding the use of special compressing plant. The gas is stated to be purer than any other kind directly obtainable.

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[73] Fr. Pat. 480,082 (1915); *J.*, 1917, 137.

[74] Fr. Pat. 480,159 (1915); *J.*, 1917, 137.

[75] *C. T. J.*, 1916, **58**, 166.

[76] *Met. and Chem. Eng.*, 1916, **15**, 494; *J.*, 1916, 1137.

[77] Eng. Pat. 12,698 (1915); *J.*, 1916, 1160.

[78] Ger. Pats. 297,258 and 292,615 (1914); *J.*, 1917, 873.

LIME, ETC.

Magis[80] describes a kiln-shaft for the burning of limestone. The kiln is enlarged in the middle and is provided with a pipe or chimney dipping into the shaft at the top. Damp fuel is used, the steam produced and the draught carrying away the combustion products. A more elaborate device is proposed by Zimmermann and Palmer.[81] A stack, with feed, combustion, and discharge zones, has a number of gas inlets around the surface of the inner wall on a level with the burning zone and a number of air inlets entering the discharge zone. The air and gas inlets are definitely spaced and not in vertical alinement. The combustion and discharge zones are preferably divided into chambers in which the gas and the main portion of the air are introduced; further air may be admitted at the bottom of the discharge zone. The effect of exposure upon commercial lime has been studied by Whetzel.[82] Comparative tests showed that carbon dioxide penetrated to a depth of about three inches in twenty days. More water was taken up in summer than in winter, but the carbon dioxide absorption was about the same. Thin layers appear to protect the remainder. A mechanical slaker is the subject of a patent of Schofield.[83]

Huber and Poindexter[84] propose to reduce alkaline-earth sulphates such as strontium sulphate by heating to 1200°–1300° C. in a reducing flame. The sulphide thus produced is subjected whilst still hot to superheated steam. The process may be made continuous in a revolving furnace, the sulphuretted hydrogen of the second stage being used in the first. Wells[85] states that the reduction of heavy spar with carbon or hydrocarbons is too slow for commercial purposes at 750° C. Maximum yields are obtained at 1000°–1100° C., and the best results with 15–16 % carbon in muffles. The water-soluble sulphide amounted to 96 % at 1050° and 99 % at 1150° C. compared with 85–87 % in direct-fired furnaces. A high temperature with rapid reduction is superior to more prolonged heating at a lower temperature.

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[79] *J. Amer. Soc. Mech. Eng.*; *C.T.J.*, 1916, **58**, 4.

[80] Eng. Pat. 100,427 (1915); *J.*, 1916, 737.

[81] U.S. Pat 1,199,856 (1916); *J.*, 1917, 31.

[82] *J. Ind. Eng. Chem.*, 1917, **7**, 287; *J.*, 1917, 454.

[83] U.S. Pats. 1,204,699/00 (1917); *J.*, 1917, 32.

[84] U.S. Pat. 1,213,375 (1917); *J.*, 1917, 385.

[85] *J. Ind. Eng. Chem.*, 1916. **8**, 770; *J.*, 1916, 1013.

THIOSULPHATE AND HYDROSULPHITE, ETC.

Hutchins, Hargreaves, and Dunningham[86] describe a method for the production of thiosulphate from sodium sulphite and sulphur, in which the sulphur and the water used are so proportioned that a solution capable of crystallisation without evaporation is obtained. The process may be made continuous by passing a hot solution of the sulphite through an intimate mixture of solid sulphite and sulphur. The reaction may be accelerated by adding about 1 % by vol. of a hydroxide or sulphide of alkali or alkaline earth metals, any excess of sulphide or polysulphide being removed by sulphur dioxide or bisulphite. Hydrated carbonates or mixtures of anhydrous and hydrated carbonates with sulphur dioxide or sodium bisulphite may be used. Furnaces for the production of sulphur dioxide free from oxygen are described by Deschamps[87] and by Pictet.[88]

Sodium bisulphite may be precipitated from a saturated solution by sodium chloride or hydrochloric acid; this procedure is the subject of a patent by Sethk.[89] An alternative method is also given by the addition of finely ground bisulphate to normal sulphite followed by washing out the sulphate with a saturated solution of bisulphite. Hutchins, Hargreaves, and Dunningham[90] produce sodium bisulphite by the action of sulphur dioxide on hydrated sodium carbonate. The gas is freed from oxygen and trioxide by hydroxides or carbonates of alkali or alkaline earth metals and passed into a tower containing the carbonate. The carbon dioxide generated converts the upper layers into bicarbonate. Monohydrated carbonate or a mixture of anhydrous carbonate and decahydrate may be used, or, if strong solutions are preferred to the solid, the decahydrate alone.

PER-SALTS, ETC.

The growing interest in the application and consequently the production of per-salts justifies a short section in this report. The Deutsche Gold- u. Silber-Scheide Anstalt[91] propose to prepare sodium perborate from granulated borax by electrolysis in a solution of alkali carbonates, till the whole is converted to crystals of perborate. Iron acts as a retarding catalyst but the harmful effects are removed by a protective catalyst, such as stannic acid, sodium perborate itself, or sodium bicarbonate. A further patent[92] by the same firm states that the cathode may be composed of such metals as lead, iron, nickel, copper, or carbon, which alone or as compounds have a decomposing action on perborate. Except in the case of nickel, the cathode at the surface of the liquid must be protected by a coating such as platinum, varnish, or rubber solution. Aschkenasi[93] suggests the drying of per-salts prepared *in vacuo*, in air at 100°, thus improving the stability of the salts and avoiding the evolution of oxygen. Schaidhauf[94] stabilises per salts by adding silicate and gum arabic during manufacture. Henkel und Co.[95] have patented the preparation of sodium percarbonate, $2Na_2CO_3,3H_2O_2$, by treating sodium carbonate with hydrogen peroxide, in the proportions indicated by the formula, at 0°C., followed by drying *in vacuo*. A similar method is suggested by Liebknecht,[96] who causes the reaction to take place in the presence of a restricted proportion of water. The percarbonate is salted out with sodium chloride and magnesium silicate added as a stabiliser. Hydrogen peroxide is produced by Cobellis[97] by heating a solution of ammonium persulphate and bisulphate. The process is made continuous by electrolysing a solution of ammonium sulphate at comparatively low temperatures to form the per-salt, heating under pressure to form sulphate and hydrogen peroxide which is subsequently distilled off under diminished pressure in a current of inert gas. L'Air Liquide[98] propose to prepare strong solutions of hydrogen peroxide from impure solutions of it by distillation under reduced pressure, more concentrated solutions being added during the distillation. The Soc. Chem. Ind. in Basle[99] produce a solid containing 27 % of peroxide by causing three molecules of hydrogen peroxide to react with one of sodium pyrophosphate. An interesting class of substances—ozonates—is obtained by Traube[100] by the interaction of ozone and alkali hydroxides.

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[86] Eng. Pat. 12,599 (1915); *J.*, 1916, 1059.
[87] Eng. Pat. 100,939 (1916); *J.*, 1916, 963.
[88] Fr. Pat. 480,294 (1915); *J.*, 1916, 137.
[89] Eng. Pat. 8,877 (1915); *J.*, 1916, 737.
[90] Eng. Pat. 10,556 (1915); *J.*, 1916, 1015.
[91] Eng. Pat. 14,292 (1915); *J.*, 1916.

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[92] Eng Pat 100,152 (1916); *J*, 1916, 1261

[93] Ger Pat. 296,888 (1915); *J*, 1917, 872

[94] U S Pat. 1,225,872 (1917); *J*, 1917, 712

[95] Eng. Pat 100,997 (1916); *J.*, 1916, 963

[96] U S Pat. 1,225,832 (1917); *J*, 1917, 712

[97] U S Pat 1,195,560 (1916); *J.*, 1916, 1059

[98] Fr Pat 478,167 (1914); *J.*, 1916, 1156

[99] Eng Pat 15,749 (1915); *J.*, 1916, 1015

[100] *Ber.*, 1916, **49**, 1670; *J.*, 1916, 1015.

HYPOCHLORITES, BLEACHING POWDER, ETC.

Haworth and Irvine[101] produce a liquid containing about 2% of hypochlorous acid by passing chlorine into water containing a catalyst, preferably a salt or oxide of copper, but nickel or cobalt may be used. The liquid may be freed from copper by precipitation or by distilling off the acid. Faust[102] prepares a saturated solution of chlorine continuously by introducing the gas and water separately into the space between the two cylinders of an apparatus consisting of an inner cylinder, with blades projecting outwards, rotating within an outer cylinder provided with freely swinging plates attached to the inner wall, so arranged that the blades come into contact with the swinging plates. Elledge[103] makes the observation that the pink coloration of sodium hypochlorite solutions prepared from bleaching powder and sesquicarbonate is due to manganese and not ferrate. If carbonate or sulphate is used, green solutions becoming pink with bicarbonate are produced. Whitehouse[104] suggests the preparation of phosgene by passing carbon monoxide into liquid chlorine at temperatures below −34° C.

Schutz[105] compares the relative efficiencies of absorbing chambers and mechanical apparatus for the manufacture of bleaching powder. The chamber process is less healthy for the workers and requires more labour and space than the mechanical process, but the latter requires more skilled supervision. For 20 tons per 24 hours four chambers require for filling and emptying, 6 men and one boy, the equivalent capacity in mechanical cylinders, 5 men and one boy. The chamber area, 2400 sq. metres, mechanical plant, 250. The capital cost is probably in favour of the mechanical type. Dry chlorine is especially essential for cylinders and the carbon dioxide must be reduced to a few tenths per cent. Dehydration by cooling to 0° C. has not been found satisfactory. For 20 tons per 24 hours a tower, 10 × 2m., is required, the water content being gauged by the tower temperatures. The view is expressed that mechanical plant will eventually supersede the absorption chamber system. Ishikawa[106] manufactures bleaching powder in inclined tubes, chlorine being fed in at the bottom and lime at the top, the solids being conveyed by scrapers.

Iodine is obtained from green seaweed by Vincent[107] by extraction with aluminium sulphate dissolved in sea water, which extracts the alkali iodides and leaves gelatinous organic matter as a residue. The solution on treatment with copper sulphate and sulphurous acid or sulphites, yields copper iodide.[107]

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[101] Eng. Pat. 12912 (1915); *J.*, 1916, 1059.

[102] Ger. Pat. 293724 (1915); *J.*, 1916, 1156.

[103] *Jour. Ind. Eng. Chem.*, 1911, **8**, 780; *J.*, 1916, 1013.

[104] U.S. Pat. 1231226 (1917); *J.*, 1917, 926.

[105] *Chem.-Zeit.*, 1917, **41**, 137; *J.*, 1917, 546.

[106] U.S. Pat. 1200499 (1916); *J.*, 1917, 32.

[107] Fr. Pat. 480014 (1915); *J.*, 1917, 137.

SULPHUR.

Urbasch[108] obtains sulphur from pyrites or spent oxide by distillation in a vertical retort, externally heated by producer gas, the oxygen-free products being conducted through the charge. The residue may be roasted, to yield the rest of the sulphur as sulphur dioxide, in a muffle below the retort.

GRAPHITE AND CARBIDE.

Graphite may be prepared, according to Messow,[109] from the waste lyes of cellulose manufacture by mixing them with oxides such as ferric oxide and with calcium phosphate, and exposing the mixture to a high temperature and very high pressure. The graphite so produced is converted into flake graphite by means of hot rolls. Donath[110] purifies graphite by heating with zinc in the absence of air, or by treatment with permanganate and caustic soda, followed by extraction with hot hydrochloric acid and washing with water. Lang[111] considers that caustic soda in this connection may cause change in the constitution of the graphite and prefers hydrochloric and hydrofluoric acids. A product designated "Expanded graphite" is prepared by Aylsworth[112] by covering flake graphite with an oxidising agent to produce a film of graphitic acid, then strongly heating so as to cause the particles to become distended like the leaves of a book. The Abdy Factories and Hylland[113] describe an intermediate product in the manufacture of calcium carbide obtained by coking a mixture of lime or limestone and caking coal at temperatures above 700° C. The product has powerful reacting properties and does not crumble or powder.

POTASH SALTS.

The vigorous search for sources of salts of potassium still continues. The report that rich deposits had been found near Motembo in Cuba, appears to have been grossly exaggerated, if not actually fraudulent.

[108] Ger. Pat. 294912 (1915); *J.*, 1917, 503.
[109] Ger. Pat. 297075 (1915), *J.*, 1917, 873.
[110] *Chem.-Zeit.*, 1916, **40**, 579; *J.*, 1916, 838.
[111] *J.*, 1916, 1259.
[112] U.S. Pat. 1191383 (1916); *J.*, 1916, 927.
[113] Eng. Pat. 14486 (1915); *J.*, 1916, 963.

The deposits were stated to contain up to 40 % of K_2O, but the Cuban Government found the highest reasonable result of the examination of thirteen samples to be only 0·51 %[114], two samples appeared to have been liberally doped with potassium sulphate. Hutchinson[115] draws attention to the following considerations of the natural saltpetre industry: (1) The present sources are not fully utilised; (2) artificial nitre-beds would probably be useful in Bihar owing to the suitable conditions; (3) present methods require investigation to improve the recovery and the conditions of trade.

The conditions of the equilibrium $KCl + NaNO_3 \rightleftharpoons KNO_3 + NaCl$ have been studied by Reinders.[116] In practice a slight excess of sodium nitrate is desirable, and after heating to 100° C. and removing the sodium chloride, the addition of water prevents the separation of further salt and saves subsequent washing. Miyama[117] states that the cost of potassium chloride from seaweed is less than £4 per ton, and notes that some are rich (0·6 % on dry weight) in iodine. Nishimura[118] gives the annual production of bittern in Japan as 240,000 tons, the composition being: magnesium chloride 12–20 %, potassium chloride 2½–3½ %, magnesium bromide ¼–½ %, magnesium sulphate 6–7½ %, sodium chloride 3–8 %. As much as 80 % of the potassium chloride can be recovered as 80 % muriate.

The suggestions for the manufacture and recovery of potash salts may be conveniently divided into three main groups according to the class of raw material employed: (1) Rocks such as felspars, leucite, alunite; (2) Lake and sea waters and waste lyes; (3) Flue dusts, etc.

Neumann and Draisbach[119] from laboratory results recommend equal quantities of ground felspar, lime, and calcium chloride as the best mixture, affording a 95 % recovery of the potash after heating for three hours at 650° C. They contrast this with Cushman's[120] method, which produced 47½ % in 1½ hours at 750° C. The economical aspect of potash extraction from kelp, alunite, felspar, etc., is discussed and the conclusion arrived at is that none of these processes will be able to compete successfully with the German industry. Schroeder[121] states that up to nearly 80 % of the potash may be extracted from finely ground leucite by sulphurous acid. The supply of leucite is enormous and the utilisation of the sulphurous gases from smelting works is suggested for the treatment. Other reagents suggested for recovering the potash from felspars are: (a) Bisulphate with a fluoride by Bassett,[122] (b) caustic soda by Fraser, Holland, and Miller,[123] (c) lime with water under steam pressure, extracting about 90 % at 10–15 atmospheres.[124] Rhodin[125] decomposes a mixture of ground felspar and salt by passing sulphur dioxide, steam, and air over the heated material. Sulphuric acid is condensed and the residues leached for soluble potash, the insoluble portion being used for cement.

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[114] *J.*, 1916, 1154.

[115] *Bull.* 68, *Agric. Res. Inst. Pusa*; *J.*, 1917, 709.

[116] *Zeit. anorg. Chem.*, 1915, **93**, 202; *J.*, 1916, 1058.

[117] *Kogyo-Kwagaku-Zasshi*, 1916, **19**, 1044; *J.*, 1917, 135.

[118] *J.*, 1917, 1046.

[119] *Zeit. angew. Chem.*, 1916, **29**, 313; *J.*, 1916, 1012.

[120] *J.*, 1915, 79.

[121] *J. Ind. Eng. Chem.*, **8**, 779; *J.*, 1916, 1012.

Charlton and Kaolin Products Corp.[126] propose to digest alkaline material such as glauconite with a solution of calcium chloride and milk of lime at a temperature below 190° C. at pressures below 200lb. for 2–4 hours, to produce a solution of potassium chloride. An account of a large scale investigation is given by Benham.[127] A mixture (110 tons) of felspar, coal, calcium chloride, and limestone was heated in a blast furnace. Some potassium chloride volatilised at 900° C. but the reaction was not complete till 1600° C. The chloride passed to a condenser and there met a current of steam and 90 % was obtained in a high state of purity on evaporation. The slag was moulded into pipes, tiles, and paving bricks. It is stated that the process may be adapted to utilise cement marls and either rotary or blast furnaces of a certain type may be used. Chappell[128] heats alunite in a reducing atmosphere at 650–1000° C., the sulphur is recovered and the potassium sulphate and alumina separated from the residue.

Wrinkle, Keeler, and Watterson[129] propose to treat waters containing sodium chloride, sulphate, and carbonate, as well as potassium chloride, with carbon dioxide to produce sufficient bicarbonate to form $Na_2CO_3,NaHCO_3,2H_2O$ ("urao"), which is removed as such after evaporation, and sodium chloride and sulphate at a later stage. The potassium chloride is obtained from the mother liquor by cooling and crystallisation. Hof[130] draws attention to the fact that on agitating waste lyes containing potassium and magnesium sulphates with finely ground anhydrous calcium sulphate, some syngenite, $K_2SO_4,CaSO_4,H_2O$, is formed, but even after 24 hours only about half the soluble sulphate is precipitated. The process for removal of sulphates from waste lyes by calcium chloride was investigated 10 years ago by Schwarz, who showed that gypsum and not syngenite was precipitated in the case of magnesium chloride liquors.

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[122] U.S. Pat. 1194461 (1916); *J.*, 1916, 1016.

[123] U.S. Pat. 1196734 (1916); *J.*, 1916, 1059.

[124] *Ross. J. Ind. Eng. Chem.*, 1917, **9**, 467; *J.*, 1917, 642.

[125] U.S. Pat. 1232677 (1917); *J.*, 1917, 1008.

[126] U.S. Pat. 1234626 (1917); *J.*, 1917, 1008.

[127] *Canadian Chem. Jour.*, May, 1917; *Met. and Chem. Eng.*, 1917, **16**, 704; *J.*, 1917, 960.

[128] U.S. Pat. 1195655 (1916); *J.*, 1916, 1016.

[129] U.S. Pat. 1184806 (1916); *J.*, 1916, 839.

[130] *Chem.-Zeit.*, 1916, **40**, 873; *J.*, 1916, 1258, and *J.*, 1914, 422.

Bassett and Spar Chem. Co.[131] describe a lengthy and complicated method of procedure to separate sodium and potassium sulphates from solutions containing 90% of the former and 10% of the latter. The description should be accompanied by a "flow sheet" for clearness, otherwise difficulty arises in following out the necessary steps in the cyclic process which is the object of the patent. Manzella[132] describes the utilisation of the mother liquors of marine salt works as a source of potassium salts. The Sicilian salt works produce annually about 167,000 cubic metres of mother liquors which are available for the production of bromine and potassium salts. An interesting group of patents by the Solvay Process Co.[133] is mentioned here, as they afford excellent illustrations of the mode of solving difficult problems of the separation of soluble salts. Magnesium and potassium chlorides are separated from brine by evaporation at low temperatures until saturated with respect to potassium chloride, the sodium chloride is removed, and by further evaporation at a high temperature the solution becomes saturated with regard to the potassium but not with regard to the magnesium chloride. On cooling potassium chloride separates. To recover the magnesium chloride evaporation at a high temperature is employed and carnallite is removed, the remaining fused product consists of 48% magnesium chloride and 52% water. The potassium chloride is removed from the carnallite by dissolving the magnesium salt in liquid saturated with respect to the potassium but not to the magnesium chlorides. The process may be carried out by causing the fractional crystallisation to take place in a series of vessels maintained at increasing temperatures, the solution circulating from the vessel of highest temperature to that of the lowest, and the salts being transferred in the opposite direction. The final products are thus produced at each end. The treatment of natural alkali deposits to separate the various constituents, including the potash, is also described.

Cranfield[134] gives the total acid-soluble potash in twelve typical samples of blast furnace dust as 2·97–15·89% and the water-soluble potash as 1·23–9·25%, the salt from the aqueous extract showing

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[131] U.S. Pat. 1194465 (1916); *J.*, 1916, 1261.

[132] *Annali Chim. Appl.*, 1917, **7**, 1; *J.*, 1917, 453.

[133] U.S. Pats. 1215546, 1215574/5/6 (1917); *J.*, 1917, 454.

[134] *J. Bd. Agric.*, 1917, **24**, 526; *J.*, 1917, 1006.

39·74–41·84 %. As a result of the employment of the Cottrell precipitator practically the whole of the potash in blast furnace dust can be obtained, this "dry cleaning" method may lead to the reclamation of many thousands of tons of potash now lost.

Huber and others[135] suggest leaching out the potash salts from cement kiln flue dust at temperatures above 85° C. to prevent the formation of $CaSO_4,K_2SO_4,H_2O$.

Treanor[136] points out that the potash content of clays and shales suitable for cement manufacture varies up to 2·5 %. A process to increase the production of potash from the clinker has been devised. By the addition of 0·8 % of fluorspar for every 1 % of K_2O the resulting potassium fluoride is readily volatilised, but is converted into sulphate by the oxides of sulphur in the combustion gases. The hydrofluoric acid is neutralised by the lime compounds present in the dust, re-forming calcium fluoride, and after leaching at a minimum temperature of 85° C., the filter-cake is returned to the kiln. In this way 90 % of the orginal potash is volatilised, of which 80 % is caught in the dust collectors. The yield is reduced a further 5 % in the leaching process. At Hagerstown,[137] 20–25 tons of dust containing 5–10 % of potash is reclaimed every 24 hours by a Cottrell precipitator working in conjunction with cement kilns.

ZINC AND LEAD COMPOUNDS

The extraction of zinc is in many cases a "chemical" rather than a metallurgical process, and hence is included in this section. The Metal Recovery Co.[138] describe the treatment of an ore containing zinc and lead sulphides which, after admixture of iron ore, is ground in the presence of concentrated zinc sulphate liquor. The sands are roasted to produce zinc sulphate, and if the iron content is low iron oxide from a previous roast is added to the charge to accelerate the formation of sulphur trioxide and thus increase the zinc sulphate content. The roasted and partially cooled material is extracted with dilute sulphuric acid to dissolve the basic zinc sulphate and zinc oxide. The iron in the leaching liquor is removed by adding zinc oxide and blowing with hot air. The precipitated iron oxide helps to bind the residual lead ore and improve it for further blast furnace treatment. If there is much iron present in the ore, excess of acid is used in the leaching, the iron is oxidised and unroasted slimes added and stirred in:—

$$Fe_2(SO_4)_3 + ZnS = 2FeSO_4 + ZnSO_4 + S.$$

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[135] U.S. Pat. 1220989 (1917); *J.*, 1917, 503.

[136] *Met. and Chem. Eng.*, 1917, **16**, 701; *J.*, 1917, 961.

[137] *J.*, 1917, 327.

[138] Eng. Pat. 12799 (1915); *J.*, 1916, 1260.

This reaction is carried out under a pressure of $\frac{1}{2}$–1 atmos. in presence of excess of zinc sulphide. The zinc sulphate liquor may be evaporated and the residue roasted and extracted with dilute acid to eliminate iron, or treated with more acid and evaporated for zinc sulphate crystals. The mother liquor, rich in iron, may be used for treating more slimes, or purified from iron by the zinc oxide contained in the sulphated roast. Ferraris[139] prepares zinc sulphate from roasted and desulphurised ore by treatment with sulphur dioxide from the roasting of sulphide ore. The sulphite is converted into sulphate by treatment with moist air. The processes may be combined. A paper of considerable length is contributed by Ridge[140] upon the utilisation of the sulphur contents of zinc ore. The description contains many illustrations, and the history of furnace development relative to this subject.

The Patent Corporation and Thompson[141] propose to produce a litharge particularly suitable for white lead manufacture, by spraying molten lead into a stream of hot air, impinging at right angles, whereby the whole is oxidised. The heat of the dust cooling chamber heats the air for the spray, and that from the melting pot the pipe to the atomiser.

ALUMINIUM COMPOUNDS.

The number of references to these compounds has been large, consisting mainly of patents for aluminates, nitride, and nitrogenous products taken out by the Mineral Products Corporation of New York. Other patents with points of more general interest are included under this heading. Llewellyn and Spence[142] propose the purification of crude aluminium sulphate prepared from bauxite and sulphuric acid by treatment under certain conditions with sodium, potassium, or ammonium salts, to precipitate the iron as a basic salt. Ramsay and Lowe[143] treat the residues from bauxite, after the removal of most of the alumina, with wet or dry carbon dioxide, to render both the alumina and soda soluble. Tone and the Carborundum Co.[144] describe the preparation of crystalline fused alumina for abrasive purposes. Bauxite, with or without the addition of carbon, is heated in an electric furnace to a temperature much above the melting point, and run off into a mould; the solid product is ground and consists of crystals of alumina, mainly 0·1–0·3 mm., and a uniformly distributed "residual basis" composed mainly of compounds of titanium, iron, and silicon.

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[139] Fr. Pat. 480409 (1915); J., 1917, 137.

[140] J., 1917, 676.

[141] Eng. Pat. 100069 (1916); J., 1917, 385.

[142] Eng. Pat. 10166 (1915); J., 1916, 889.

[143] Eng. Pat. 9705 (1915); J., 1916, 963.

[144] U.S. Pat. 1192709 (1916); J., 1916, 1261.

TITANIUM COMPOUNDS.

References under this heading are of great interest owing to the far-reaching effects which success in the utilisation of the enormous deposits of titaniferous material, hitherto almost useless, would have on the iron industries. Rossi and Titanium Alloy Manufacturing Co.[145] propose to fuse ilmenite with sodium bisulphate, boil with water and acid until the titanium dioxide is dissolved, filter off the insoluble matter and boil again to precipitate the titanium. From the number of patents[146] taken out by the Company with a view to improvements in the method of working titaniferous material, the problem would appear to be a difficult one, a fact which many investigators in this field will heartily substantiate.

The "National Tidende" reports that titanium ore is being worked at Frederikstad.

RADIUM, ARGON, ETC.

Schlundt[147] extracts 90 % of the radium of low grade carnotite ore, containing 4·88 parts per billion, by sulphuric acid of 78 % or over. Vanadium and uranium require 35 % acid for extraction. High grade ore with 42·78 parts per billion was also successfully treated. The temperature appears to be of far less importance than the concentration of the acid. The use of cobalticyanides for the separation of yttrium from erbium, or the resolution of mixtures containing dysprosium, holmium, and yttrium, with traces of erbium, terbium, and neodymium, is recommended.[148] Speter[149] separates scandium from other rare earths by precipitation as an insoluble hypophosphate, which is then decomposed by sulphuric acid and the scandium precipitated as oxalate. Browning and Spencer[150] describe the separation of caesium and rubidium by the fractional crystallisation of the iron and aluminium alums. Grant and Jones[151] decide that the fractional precipitation of the earths of the yttrium group by ferricyanides is the most rapid method yet known. The double oxalates and the methyl-, ethyl-, and triethylamine methods have been examined, but are not suitable for the fractional crystallisation of this group.

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[145] U. S. Pat. 1184131 (1916); *J.*, 1916, 738.

[146] U.S. Pats. 1171542, 1189229, 1196029/30/31; 1206796/7/8 (1916), 1235638 (1917); *J.*, 1916, 839, 890, 1016; 1917, 84, 1047.

[147] *J. Phys. Chem.*, 1916, **20**, 485; *J.*, 1916, 690 and 837.

[148] *J.*, 1916, 926.

[149] Ger. Pats. 282657 (1911), 292257 (1912); *J.*, 1916, 927.

[150] *Amer. J. Sci.*, 1916, **42**, 279; *J.*, 1916, 1014.

[151] *J. Amer. Chem. Soc.*, 1917, **39**, 933; *J.*, 1917, 711.

Argon is obtained by Filippo and others[152] by passing cooled compressed air downwards through a rectifying column and bath of boiling oxygen at the base. The liquid air flows over to the higher part of the column, the interior of which consists of an inner chamber with draw-off cocks at different levels. In this the mixture is separated into purer oxygen and a rich argon mixture which can be used for electric lamps. Fonda and General Electric Co.[153] produce a liquid with 94% oxygen and 4% argon, and fractionate it on the counter-current principle in such a manner that argon is removed at the top and oxygen at the bottom of the apparatus.

ACETIC, FORMIC, AND OXALIC ACIDS

Harburger Chem. Werke[154] suggest the concentration of dilute acetic acid by mixing with potassium acetate so as to form double compounds which may be separated, and the acid recovered by distillation. The potassium acetate may be partially replaced by other dehydrating salts, such as calcium chloride. A new form of decomposing unit for acetates is described, in which a mixture of acetate and sulphuric acid is fed on to the surface of a rotating drum and the solid products removed by a scraper.

The Holzverkohlungs Akt.-Ges.[155] and also Gorham[156] have patented a method of much interest for producing a purified acetic acid. To a mixture of about equal parts of crude acetic acid and 70% sulphuric acid at a temperature of 150° C., crude acid is continuously added to replace the purified acid which is distilled off. A certain proportion of water must be maintained to prevent the destruction of the acetic acid by the sulphuric acid.[157] Concentrated aqueous solutions of soluble sulphates may be employed as diluents instead of water. Zinkeisen and Fore Chemical Works[158] suggest the removal of organic impurities from crude calcium acetate by boiling with a mixture of lime, iron salt, and a bleaching agent. A rapid process for the complete oxidation of acetaldehyde by air or oxygen is described by the Badische Co.[159] The catalysts suggested are iron salts and the organic salts of alkalis or alkaline-earths, including those of aluminium and magnesium. Hibbert and Union Carbide Co.[160] produce acetic acid by the oxidation of acetaldehyde in the presence of wood charcoal saturated with strong acid. Katz and Ovitz[161] prepare formates from caustic alkali solutions by the action of carbon monoxide and volatile alkali such as ammonia. A descending stream of the caustic alkali meets the ascending gases in a closed vessel at 10–20 atmos. and 150°–200° C. The conditions of the production of hydrogen from calcium formate have been investigated by Levi and Piva.[162] In the presence of steam, carbon monoxide acts on slaked lime to produce formate at 250°–300° C., and carbonate and hydrogen above 300° C.; the reaction is slower than with caustic soda. At 500°–600° the formation of hydrogen is almost quantitative if water is present. In the presence of even small quantities of caustic soda it is possible to obtain a 50% yield of hydrogen at 300°. Two patents[163] by Portheim relate to the production of oxalic acid from sugar or other carbohydrates by means of nitrogen oxides. Either molybdenum or vanadium or both may be employed as catalyst Overheating of the materials is avoided by a preliminary treatment with the gases, and temperature regulation is achieved by regulating the rate of flow.

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[152] Eng. Pat. 101860 (1916); J., 1917, 32.
[153] U. S. Pat. 1211125 (1917); J., 1917, 215.
[154] Ger. Pat. 292950 (1915); J., 1916, 962.
[155] U. S. Pat. 1196229 (1916); J., 1916, 1059.
[156] Eng. Pat. 107606 (1916); J., 1917, 962.
[157] U. S. Pat. 1210792 (1917); J., 1917, 214.
[158] U. S. Pat. 1213724 (1917); J., 1917, 386.

Thorssell and Lundén[164] manufacture oxalic acid from sodium oxalate containing sodium carbonate and hydroxide by treatment with a solution of sodium bisulphate and sulphuric acid to produce sodium oxalate and sulphate. The acid oxalate is then washed with water and treated with sulphuric acid to produce oxalic acid and a solution of bisulphate and sulphuric acid for further use with the crude oxalate. Dugan[165] obtains sodium or other oxalate by spraying the metal into a pebble mill in which a heated atmosphere of carbon dioxide is maintained. A possible use for the waste liquor from paper pulp is suggested by Reed.[166] After drying, 100 parts of the residue is mixed with 300 parts of concentrated nitric acid and the temperature maintained at 95° C. After removal of the excess of nitric acid and water by heat, the oxalic acid is recovered by crystallisation. The actual mechanism of the formation of oxalates from formates is not known with certainty; the following suggestions have been made:—

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[159] Ger. Pat. 284724 (1914); *J.*, 1917, 503

[160] U.S. Pat. 1230899 (1917); *J.*, 1917, 925

[161] U.S. Pat. 1212359 (1913); *J.*, 1917, 385

[162] *Annali Chim. Appl.*, 1916, 5, 271; *J.*, 1916, 926

[163] Eng. Pats. 101680, 14234 (1915); *J.*, 1916, 1156 and 889

[164] Eng. Pat. 11487 (1915); *J.*, 1916, 962.

[165] U.S. Pat. 1232249 (1917), *J.*, 1917, 026.

[166] U.S. Pat. 1217218 (1917); *J.*, 1917, 503.

$$2HCOONa = C_2O_4Na_2 + H_2 \text{ at } 440^\circ C;$$
$$2HCOONa = Na_2CO_3 + CO + H_2 \text{ at } 360^\circ C,$$

and the doubtful reaction—

$$Na_2CO_3 + CO = C_2O_4Na_2,$$

which is perhaps the expression of the Goldschmidt method of heating four parts of formate with five of carbonate in lead vessels to 400°–410°. Some have thought that

$$HCO_2Na + Na_2CO_3 = C_2O_4Na_2 + NaOH$$

represents the reaction, and it has been claimed that by the use of sodium oxalate as a diluent a 95% yield is obtained when using 40% of oxalate. Hempel[157] suggests the production of oxalate without the isolation of formate. The conversion may be affected *in vacuo* at 280° C. and the hydrogen recovered.

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[157] Fr. Pat. 389039 (1908).

GLASS, REFRACTORY MATERIALS, CERAMICS, AND BUILDING MATERIALS

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GLASS

THE prescient and energetic policy of the Department of Optical Munitions and Glassware Supply of the Ministry of Munitions has been of great advantage to the general glassmaking industry of this country. Every encouragement has been given to the application of scientific methods of manufacture and to the adequate co-operation of pure scientists with the industry. In consequence, much has been done to place the industry in a position to cope with the present abnormal conditions and with the probable great trade activity which will follow the war. The successful inauguration of the Society of Glass Technology is indicative of the greater interest which is being taken in the scientific aspects of glass manufacture. Much good would result to the industry as a whole if some scheme for the pooling of technical knowledge could be arranged. There are obvious difficulties in the way of such interchange, but much duplication of research and experimental work could probably be thus avoided.

Resistant glassware suitable for analytical operations was first introduced by Schott, of Jena, in 1892, and improvements in the quality of this glass were made a few years before the war. In recent years a number of other types of resistant glassware of American, German, and Austrian manufacture have been obtainable, and since the outbreak of war there has been considerable activity in the manufacture of the resistant ware in countries cut off from German and Austrian supplies. Much progress can be recorded in this country, as also in France, America, and Japan, and supplies of glass of satisfactory durability are now available. In general this glassware resists attack quite as well as, and in some cases better than, the best German laboratory glass, but it is necessary that increased attention should be given to the annealing so that the desired improvement in mechanical properties is forthcoming. Cauwood, English, and Turner[1] have investigated the attack of chemical reagents on glassware of English manufacture, and concluded that high boric oxide content confers resistance to water attack but renders the glass vulnerable to attack by alkalis and acids; that alumina bestows resistant power towards sodium carbonate, and that high silica content is necessary to give protection against attack by acids. Four glasses of English manufacture were found to be superior in resistant power to Jena glass, and the following analyses of them are given:

Glass	SiO_2	Al_2O_3	ZnO	CaO	MgO	K_2O	Na_2O	B_2O_3	MnO	Fe_2O_3
C	65.45	6.18	9.00	0.4	trace	0.31	11.81	7.13	-	0.09
D	66.51	6.74	3.62	4.35	0.33	2.78	11.52	4.57	0.10	0.08
E	66.38	6.60	8.66	0.40	0.12	1.69	10.03	6.92	trace	0.12
G	69.40	1.00	7.65	5.78	trace	7.92	6.36	4.01	0.08	0.12
Jena	64.58	6.28	11.78	0.08	0.12	trace	7.38	10.03	trace	0.10

The molecular proportions of acid constituents (silica and boric oxide) to bases are, C 3.2 to 1, D 2.85 to 1, E 3.4 to 1, G 3.3 to 1, Jena 3.7 to 1. It was found that of the glasses tested the least durable were those that departed most from the 3 to 1 ratio.

P. Nicolardot compared the resistance to attack of three glasses of French manufacture with German glasses and concluded that the former were quite equal to the latter. Their thermal endurance, which was tested by plunging flasks full of hot paraffin wax into cold water, was not so satisfactory.

A standard test for chemical resistivity is desirable, and it is probable that the most useful single test is to expose the glass to the action of water and steam at high temperatures in an autoclave and determine the loss in weight and the residue on evaporation. Exposure for three hours at a temperature of 180° C. with a pressure of about 10 kilos per sq. cm. would, in the writer's opinion, be an efficient test. Probably liquid water is a more potent agent than steam in attacking glass.[3] C. Barnes[4] found that at temperatures just above 185° C. liquid water attacked glass very rapidly, with the separation of hydrated silicic acid.

Since the war there has been a great shortage of heat-resisting glass lampware previously exported in large quantities by Germany and Austria. The special properties of this glass depend primarily on the possession of a low coefficient of expansion. Glassware suitable for use in high pressure gas and oil incandescent burners, arc lamps, etc., of quite satisfactory thermal and mechanical endurance, is now being made in this country, and when the necessary skilled labour is available supplies should be adequate to meet the demand.

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[1] *Jour. Soc. Glass Tech.*, 1917, **1**, 153; *J.*, 1917, 873.

[2] *Comptes rend.*, 1916, **163**, 355; *J.*, 1916, 1156.

[3] See, Mellor, "Plasticity of Potters' Materials."

[4] *Amer. J. Sci.*, 1889, **38**, 407, and 1891, **41**, 110.

E. C. Sullivan and W. C. Taylor[5] have developed a borosilicate glass of high silica content with a mean linear coefficient of expansion between 19° and 350° C. of 0·0000032. This glass also has a very low reflectivity for radiant heat and is being developed for culinary purposes. E. C. Sullivan[6] considers that the difficulty in obtaining glass of low coefficient of expansion is to a great extent due to the decreased fluidity at founding temperatures, and that the drawbacks in the use of boric oxide are that it reduces the stability of the glass and that the reduction in expansibility is not continuous but reaches a minimum. He suggests the determination of a coefficient of thermal endurance, instead of the coefficient of expansion, by heating pieces of the glass in rod form to a definite temperature in a vertical electric furnace, and dropping them simultaneously into water, the temperature at which 50 % of the rods fracture being used as a standard of comparison of thermal endurance. Progress can be recorded in the manufacture of bulbs for incandescence electric lamps and automatic machinery capable of large outputs is now in use.

The work of the Glass Research Committee of the Institute of Chemistry has continued, and formulæ for numerous special glasses have been communicated to manufacturers through the Ministry of Munitions. Research work has also been in progress at the National Physical Laboratory and in the Department of Glass Technology of the University of Sheffield.

Noteworthy progress has been made in the production of optical glass, and a list recently issued by Chance Bros. and Co., Limited, is indicative of much successful work in the manufacture of types of glass for which opticians were formerly dependent on the Jena works.

Williams and Cox[7] describe experiments made with a series of 42 barium glasses with a molecular composition ranging from 2·5 to 5·5 SiO_2, 0 to 0·5 Na_2O, 0 to 0·5 BaO, with 0·1 ZnO and 0·4 K_2O. Note is made of the working properties, density, coefficient of expansion, solubility, liability to devitrification, softening point, and viscosity range. Potash-barium glasses of maximum barium content were made having a lustre equal to that of potash-lead glasses used for the best quality of cut glass. L. Springer[8] has continued his search for efficient substitutes for the nitrates of potassium and sodium referred to in the previous report, and a further account is given of laboratory trials with barium peroxide. The colouring effect of iron in lime glasses was greatly diminished by its use, but in lead glasses it was not advantageous. Reference has been made[9] to the rapid attack on glass pots when barium peroxide is used in excess. It is stated that by the substitution of graphite for a portion of the grog in the clay mixture from which the pots are made a more resistant material is obtained. The same author[10] considers that nickel oxide should be the most suitable decolorizer to use in glass made from a salt-cake batch.

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[5] *J. Ind. Eng Chem.*, 1915, **7**, 1064 ; see also *J.*, 1916, 513.

[6] *J*, 1916, **35**, 513.

[7] *Trans. Amer. Ceram. Soc.*, 1916, **18**, 315 ; *J.*, 1917, 712.

Turner and Cauwood[11] have investigated the effect on the glass of impurities present in Russian potash. When the batch was melted at 1300° C. sulphate to the extent of 0·25 % of the batch and chloride to the extent of 0·5 % caused opacity if the molten glass remained at about 1000° C. for a few hours. Phosphate to the extent of 1 % of the batch did not produce milkiness. The milkiness could be retarded by the presence of borax, in which case it reappeared on reheating or by melting at a high temperature.

In a discussion on the melting of lead glass in open pots,[12] attention is directed to the use of a washed gas with the proportions of gas and air controlled to give an oxidising atmosphere in the furnace. To prevent rapid deterioration of the glass in successive melts it is considered desirable to use for the manufacture of the pots a plastic clay giving a dense, vitreous body on burning. The wear on such pots is more uniform and "wreathy" glass is avoided.

G. T. Morgan[13] suggests a method for the utilisation of nitre cake in glass manufacture by using a batch containing the nitre cake with wood charcoal, sand, and limestone, and recovering the sulphur by connecting the furnace to a sulphuric acid plant. In laboratory experiments the efficiency of sulphur recovery was about 66 %.

Rosenthal[14] has made a series of experiments on the artificial coloration of glass by exposure to light of short wave lengths. A Coolidge vacuum tube was used as the source, giving a current of 100 milliamperes at 50 kilovolts. Thin colourless glass is coloured uniform tints by this exposure, but glass over 0·25 inch thick shows a gradation of colour from the exposed side. The coloration of porcelain teeth in this way is suggested. If the composition of the white glass is known, the resulting colour may be predicted.

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[8] *Sprechsaal*, 1917, **50**, 49.

[9] *Sprechsaal*, 1916, **49**, 34.

[10] *Sprechsaal*, 1916, **49**, 208.

J. Soc. Glass Tech., 1917, **1**, 87 ; *J.*, 1917, 387.

Sprechsaal, 1916, **49**, 303.

Econ. Proc. Roy. Dublin Soc., 1917, **2**, 238 ; *J.*, 1917, 504.

J. Ind. Eng. Chem., 1917, **9**, 734 ; *J.*, 1917, 1009.

The development of electric steel melting furnaces in this country is directing attention to the necessity for the provision of suitable eye-protecting goggles for those engaged in working the furnaces. The choice of suitable goggles for a workman necessitates investigation of the physical characteristics of the light to which he is exposed. In recent years a great deal of work has been done with the object of producing glass which will effectively filter out any desired rays. The researches of Sir William Crookes[15] have already found some commercial application in the production of glasses which transmit a great deal of light but are opaque to the ultra-violet rays. These glasses, whilst they fulfil a useful purpose, are, however, not dark enough for most of the trades which demand goggles. Luckeisch, of the Nela Research Laboratories,[16] suggests as a general solution of the problem the combination of a yellow-green glass totally absorbing ultra-violet rays with a shade of smoked neutral glass sufficiently dense to reduce the brilliancy of the light to a safe degree. It is desirable that the glass which is used should not modify colour perception to any considerable extent, and that the infra-red as well as the ultra-violet radiation should be filtered out. In view of the fact that in the radiation from the surface of molten glass the infra-red rays are present in far greater abundance than the ultra-violet, it is inferred that glassworkers' cataract is to be ascribed to the heat rays rather than to the ultra-violet. Exposure to radiation rich in ultra-violet is an important factor in the causation of conjunctivitis. Coblentz and Emerson,[17] in an investigation of protective glasses, conclude that for absorbing the infra-red rays deep black, yellowish, green, gold plated, sage-green, and bluish-green (ferrous iron) glasses are efficient. Of the infra-red rays emitted by a furnace at 1100° C. about 99 % are absorbed by gold plated glass, 95 % by sage or bluish-green glass, 60 to 80 % by deep black glass, and about 60 % by greenish-yellow glass. Several minerals,[18] for example beryl and garnet,

$$[Ca_3 (FeMg)_3 Al_2 (SiO_4)_3],$$

have been found to be very opaque to the infra-red rays.

Attention has been given by several investigators to the phenomena of annealing. Twyman[19] points out that the phrase "want of annealing" as applied to glassware means the presence of internal stress. The stress cannot originate in glass at either high or low temperatures, but at an intermediate range of temperature internal stresses may be set up which may take something of the order of some minutes, an hour, or a few hours to die out. This "annealing range" is all important, and an accurate knowledge of the mechanical properties of the glass throughout is necessary if good annealing is to be obtained in a minimum of time. It is shown that within this range the mobility (the converse of viscosity) doubled for each 8° C. rise in temperature. A law of change of viscosity with temperature is deduced which holds in the case of all the glasses examined. An apparatus called the Hilger Strain Meter is described which depends on the following facts. A beam of light in its passage through strained glass is doubly refracted, and this double refraction can be detected by a polarimeter, the existence of strain being revealed by the presence of light and dark bands on the object according to the nature and amount of strain present. An addition to the apparatus of a wave plate was suggested by F. E. Lamplough, and regions of stress are then marked out as a colour contrast effect; well annealed specimens produce no change in the colour of the purplish-pink background, while regions of stress become a light blue or yellowish red according to the direction of the stress, the brilliance of the colour contrast being an indication of the intensity of the stress. With this apparatus glass objects can be examined rapidly, any stress of importance being revealed at once. It is suggested that as a standard of annealing there should be present in the finished article no stress amounting to one-twentieth of the breaking strain of the glass. An average compressive stress of [illegible]0 to 300 kg./cm.^{2} and an average tensile stress of half that amount was found in a number of badly annealed flasks and beakers examined and fully accounts for their liability to sudden fracture. A method and apparatus is described by which the annealing temperature of any glass can be determined with an accuracy of ± 3° C. The routine is established by a theoretical argument and results checked by the actual annealing of glass vessels. There is a very considerable difference in the annealing temperatures of different kinds of glass, and it is of great importance that glass manufacturers should give attention to this and not attempt to pass through the lehr simultaneously glasses of varying compositions. Turner[20] draws attention to the thickness of the article being an important factor in determining the rate of passage through the lehr and to investigations proceeding on the conditions of annealing.

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[15] *Phil. Trans.*, 1914, 214.

[16] *Archives of Ophahtlmology*, July, 1914.

[17] *U.S. Bureau of Standards, Tech. Paper* No. 93, 1917 ; *J.*, 1917, 647.

[18] *Carnegie Institute of Washington, Publication* No. 65, 1908.

[19] *J. Soc. Glass Tech.*, 1917, 1, 61 ; *J.*, 1917, 339.

English[21] describes optical and mechanical methods of determining annealing temperatures, and shows that the annealing temperature of glass is below the temperature of softening. The times required for stress to disappear in a glass examined were 570 minutes at 550° C., 270 minutes at 600° C., 18 minutes at 625° C., and 10 minutes at 650° C.

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[20] *J. Soc. Glass Tech.*, 1917, **1**, 74.

[21] *J. Soc. Glass Tech.*, 1917, **1**, 74; *J.*, 1917, 339.

Parker and Dalladay[22] describe a method for the union by heat treatment of glass surfaces in optical contact. The glass surfaces are placed in optical contact under moderate pressure and kept for about 1¼ hours at a temperature 70° to 80° C. below the annealing temperature as determined by the method of Twyman. It is necessary that the annealing temperatures of the two glasses should not differ by more than 50° C.

P. G. H. Boswell[23] has made an exhaustive survey of British resources of sand suitable for glass-making. It is impossible to over-emphasize the importance of an adequate study of our home resources of the naturally occurring materials used either directly or indirectly in the manufacture of glass. In pre-war days large quantities of glass sand were imported into this country from Belgium and France. These sands were very suitable for their purpose and were cheap, as they were usually brought over in coal boats as ballast. The author shows that while we have not in this country any deposit equal in quality, uniformity, and extent to that of Fontainbleu, we have ample supplies of sands suitable for all ordinary glasses. The properties desirable in a glass-sand are dealt with in detail. It should be uniform in size of grain, and experience has shown that the sands behaving best during glass melting are those containing a large proportion of grains from 0·25 to 0·50 mm. in diameter. The presence of very fine grains causes the production of small "seeds" which are difficult to remove in the fining process. An even grade is also an important factor in securing homogeneity and it is improbable that stirring completely eliminates the heterogeneity caused by the use of badly graded and unevenly melting sands. The methods of determining the grading of a sand by mechanical analysis are discussed, and in the supplementary memoir details are given of a satisfactory elutriator constructed from wide glass tubing only. Consideration is given to the chemical composition of the sands and to the effect of impurities on the melting process and the resultant glass. It is suggested that the limits of iron oxide content for various glasses are:—Optical glasses carrying barium and zinc, below 0·02 %; crown optical glass, up to 0·04 %; crystal flint glass,

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[22] Faraday Society, Dec. 18, 1916; *J.*, 1917, 32

[23] Memoir and Supplementary Memoir on British Resources of Sands suitable for Glassmakers.

British Glass-sands. *J. Soc. Glass Tech.*, 1917, 1, 3; *J.*, 1917, 216.

0·02 %; laboratory, medical ware, and plate glass, 0·05 %; window glass 0·10 %. In the opinion of the present writer it is not possible to produce a crown glass with sufficient freedom from colour with a sand containing 0·04 % of iron oxide, although it has been stated that certain kinds of optical glass may be successfully made from sands containing that amount of impurity and without the use of decolorizers. The value of alumina in a sand is discussed and attention directed to its advantage in a bottle glass as it renders the glass tougher and better able to withstand pressure. The opinion is rapidly gaining ground that, far from having a tendency to cause devitrification, alumina in moderate amount has just the opposite effect, and will prevent devitrification. Experiments made by W. E. S. Turner have shown that when alumina is added to a window glass batch, the resulting glass does not devitrify when heated in a blowpipe flame. Investigations made by Singer[24] indicate that in a glass batch containing alumina it is possible to reduce the cost of production by increasing the sand and lime at the expense of the alkali. The importance of a mineral analysis of a sand as a means of controlling consignments and of indicating impurities is referred to. Heavy detrital minerals such as zircon, magnetite, hæmatite, limonite, ilmenite, sphene, and rutile should be present in small amounts only. The proportion of these heavy minerals was found to increase with decrease in grade size. The possibility of using crushed quartzites and other rocks is considered, but economic reasons will prevent the extended use of these materials in this country. The author also surveys our resources of suitable rocks of low iron content which might be substituted for the felspar which is imported from Scandinavia. It is unfortunate that the only known deposits of any extent are in such inaccessible situations. By means of a geological map the position of English sand deposits relative to the centres of glass industry is illustrated.

Peddle[25] obtained excellent results with washed British sands, and draws attention to the need of proper scientific treatment of British sands and the desirability of their supply to the glass manufacturer ready for immediate use. A detailed investigation of the sand occurring at Huttons Ambo in Yorkshire was made and shows to how great an extent a sand may be improved by adequate treatment. Melts made with sand from Muckish Mountain, Donegal, gave colourless glasses which were indistinguishable from glasses made with the finest continental sands. It is therefore possible that despite the inaccessibility of its occurrence this sand may provide a home supply of the comparatively small quantities of sand required for the manufacture of optical glass.

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[24] *Keram Rundschau*, 1915, 5; *J.*, 1917, 873.

[25] *J. Soc. Glass Tech.*, 1917, 1, 27, *J.*, 1917, 216.

Teisen[26] reviewed the development of glass furnaces on the continent and referred particularly to the Hermansen recuperative furnace in which the combustion is sufficiently under control to permit the melting of lead glasses in open pots. It is considered that from the point of view of the weight of glass melted the recuperative furnace is more efficient than the regenerative furnace. This would certainly not apply in the case of large tank furnaces, but for small sized pot furnaces the recuperative system undoubtedly presents many advantages.

REFRACTORIES.

During the year under review much work has been done in focussing the attention of both manufacturers and users on the need for specialized research on refractory materials of all types. A conference on refractories research, summoned conjointly by the Ceramic Society, Faraday Society, Institution of Gas Engineers, and the Iron and Steel Institute, was held in March and appointed a sub-committee to report on (*a*), the extent of the research work on refractories already in progress, (*b*), the facilities for research existing in this country, (*c*), the facilities existing for rendering available published information on refractory materials. At a second conference in July the report[27] of this committee was considered. It deals in detail with the requirements of refractory materials by the industries of the country, and indicates the numerous points on which research is necessary. It suggests the investigation of a number of physical, physico-chemical, and mechanical properties of refractories under service conditions. At this second conference the unanimous opinion was that it was desirable to establish a Research Association to create and operate a scheme for the co-ordination of the research work on refractory materials which is at present being carried out in different centres in the United Kingdom and to initiate such further investigations as are called for by the various industries interested in these materials, either as makers or users. It is intended that the Association shall work in conjunction with the Department of Scientific and Industrial Research. Already an important school of research in Ceramics and Refractories is in existence at Stoke-on-Trent in the heart of the pottery industry. London, Sheffield, Leeds, Birmingham, Glasgow, and South Wales have already formulated and laid plans for the execution of comprehensive schemes of research bearing on their own special requirements in refractories. It is essential that the work of these research laboratories should be carried on in close touch with the various industries so that the necessary co-ordination between laboratory results and works practice may be secured.

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[26] *J. Soc. Glass Tech.*, 1917, **1**, 74; *J.*, 1917, 383.

[27] Report of Second Conference on Refractories Research and Standardization *J.*, 1917, 952

Methods of Testing Refractories.

Nesbit and Bell[28] have used the following method for testing the resistance of refractory bricks to slag penetration. A hole 2·5 inches in diameter and 0·5 inch deep at the side is cut in the brick, using a drill pointed at an angle of 150°. The brick is then heated to 1350° C. and a known quantity of slag ground to pass a 40-mesh sieve placed in the hole. After maintaining this temperature for 2 hours the brick is allowed to cool and when cold sawn across so as to bisect the original cavity at the centre, so exposing an area of slag penetration which is measured by a planimeter. Increasing the duration of the test beyond 2 hours had no marked effect, neither had variations in the fineness of the slag. In a crushing test adopted by the same authors the brick to be tested is ground so that opposite faces are parallel, measured and heated to a temperature of 1350° C. The time taken to reach this temperature should be at least 6 hours and it should be maintained for 2 hours. The brick is then quickly placed in a testing machine of standard type, with asbestos board above and below the specimen, and the crushing weight determined.

E. and E. A. Griffiths[29] used a special form of carbon tube furnace for determining the softening points and compressive strength of refractories. It includes a device for applying pressure up to 150 lb per sq. inch to the test piece which is in the form of a cylinder ⅝ inch diameter and 1 inch long. A useful bibliography on electric furnaces, the melting and softening points of refractory materials under load, and of electric furnace products is added to this paper.

Le Chatelier and Bogitch[30] have investigated the crushing strength of fireclay bricks cold and at temperatures between 950° and 1500° C. Cubes of 1 cm. sides were supported on a block of sintered magnesia, with an intervening layer of chromic oxide, in a Schloesing gas-heated furnace, and pressure was applied by an iron rod with an end piece made of bauxite burned at 1600° C. The results they obtained were in conformity with those established by Mellor. They suggest that the quality of fire bricks may be judged by determining the temperature at which the deformation is 20 % under a pressure of 20 kilos. per sq. c.m. applied for a period of one minute. This high pressure was chosen in order to limit the experimental errors. For the materials tested the temperature of deformation lay between 1350° and 1500°C. The equilibrium range of sillimanite and tridymite in firebricks is discussed, and it is suggested that the lack of knowledge as to the nature of the fusibility curve of mixtures of tridymite and sillimanite is due to the fact that below 1500 °C. vitreous silica is not sufficiently fluid to permit rapid changes towards a state of equilibrium.

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[28] *Met. and Chem Eng*, 1917, **17**, 184; *J*, 1917, 1048

[29] Faraday Soc., Dec 18, 1916; *J*, 1917, 33.

[30] *Comptes rend*, 1917, **164**, 761; *J*, 1917, 595.

The following method for testing refractories under load at high temperatures is suggested by the American Society for Testing Materials.[31] A full-sized brick is heated under load under specified conditions and the resulting deformation measured. The furnace of special construction is heated by two tangentially disposed burners, the flames from which are isolated from the brick by an alundum cylinder. The brick rests on a carborundum block and carries another block of the same material which projects through the top of the furnace. To this projecting block the load is applied by means of a cross beam carrying weights so as to apply a pressure on the brick of 25 lb. per sq in. The specimen is raised to the test temperature in 4½ hours and maintained there for 1½ hours. The suggested testing temperatures are: for silica material, 1500° C.; first grade clay goods, 1350° C., medium grade, 1300° C.; and low grade, 1100° C. The cooling must be slow and should take at least 5 hours. The length of the brick is measured before and after test and the percentage decrease calculated.

Hancock[32] describes a simple form of apparatus for measuring abrasion at working temperatures. Two test pieces are superimposed, the lower being held firm and the upper one made to move to and fro over the lower by an arm connected with an eccentric and driven by an electric motor. Preliminary experiments indicate that actual abrasion by one clay surface upon another was least with fine grain material and that abrasion increases with the temperature.

Cronshaw[33] suggests the measurement of permeability instead of porosity because, as ordinarily determined, porosity is not necessarily a measure of susceptibility to penetration. A cube of the refractory material is to be immersed in a bath of molten slag for a specified time at a definite temperature, and the extent of penetration estimated by comparison of the original porosity with the porosity after immersion. Lessing[34] describes a simple method of elutriation for ascertaining the texture and rational composition of unburnt refractory mixtures. Comparisons of English and German gas retort mixtures are given, the latter having a much higher proportion of grog.

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[31] Amer. Soc Testing Materials, June, 1917; *J.*, 1917, 1048.

[32] *Trans. Ceram. Soc.*, 1917, **16**, 49.

[33] *Trans. Faraday Soc.*, 1917, **12**, 166; *J.*, 1917, 648.

E. Griffiths[35] describes a method for the determination of the thermal conductivity of refractories. Reference is made to the work of Wologdine[36] and to the investigations of Cobb, Dougill, and Hodsman[37] on this subject. A laboratory gas muffle heated by a Méker burner supplied with compressed air reached a temperature of 1300°–1400° C. in about 4 hours, but on covering the outer surfaces with a 2-inch layer of magnesia-asbestos composition the same temperature was attained in under 2 hours. Results obtained by using diatomaceous bricks, slag wool, and silicate cotton mats as insulating materials are detailed. Slag wool can withstand a fairly high temperature without losing its fibrous structure, but it should not be subjected to prolonged heating at temperatures much above 750° C. Reference is made to the three general conclusions to be deduced from Wologdine's work :—(1) that the conductivity increases with the firing temperature; *e.g.*, silica bricks burnt at 1300° C. have a conductivity 50 % greater than those burnt at 1050° C.; (2) that with all materials the thermal conductivity increases with the temperature, with the exception of chromite brick, in which it is nearly constant; (3) that the conductivities of carborundum (SiC, 87 %; SiO_2, 12 %) and graphite (C, 48 %; SiO_2, 30 %) bricks are of the order of 4 to 6 times those of fireclay bricks.

Fireclay Refractories.

A. A. Knox[38] condemns the rational analysis of clay as of little value and considers that more reliable results can be obtained by calculation from the ultimate analysis. The following average analysis of calcined Glenboig clay is quoted :—

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Alkalis
59·22	35·31	3·03	1·37	0·30	0·28	0·49

Large deposits are known containing up to 42 % of Al_2O_3 with a low percentage of fluxing impurities. The physical properties vary, plastic and non-plastic clays of similar composition occurring.

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[34] *Trans. Faraday Soc.*, 1917, **12**, 68; *J.*, 1916, 1219.

[35] *Trans. Faraday Soc.*, 1917, **12**, 109; *J.*, 1916, 1219.

[36] *J.*, 1909, 709.

[37] *J.*, 1915, 9.

[38] *Trans. Faraday Soc.*, 1917, **12**, 144.

Bailey[39] investigated the difficulties and causes of variation in the determination of the linear shrinkage of clay. He considers that the more reliable results are obtained by the volume method of determining shrinkage. Millsom, Robertson, and Treischal[40] studied the effect of the addition of non-plastic materials to a plastic clay on the drying and burning shrinkages and the crushing strength of the finished product.

Bains[41] suggests the possibility of using the flotation process for the dressing of clays.

Cronshaw[42] considers that the chief cause of the deterioration of bricks in open-hearth furnaces is the combination of basic flue dust and volatilised oxides with the material of the bricks. Abrasion by hot gases, rapid movement due to sudden changes in temperature, and the action of particles of slag shot up from the molten charge also assist in the destruction of the bricks, particularly of the furnace walls. To resist destruction in blast furnaces and cupolas the composition and texture of the bricks must be adjusted to suit the conditions. The main destructive influences are the deposition of carbon within the bricks themselves and the deposition of certain volatile substances in the cavities and crevices running through the brickwork. The former mainly depends on the permeability and purity of the brick as regards active compounds of iron. The deposition of carbon within the pore-spaces and the consequent secondary actions have a very detrimental effect on the coherence of the bricks. The process of substitution apparently advances progressively outwards, and as the "scar" is more friable than the original brick it easily succumbs to the abrasive action of descending charges. The inner zone of "scar" protects the unaltered brickwork from the high furnace temperature and the fluxing action of the charges, but at the same time conditions arise which favour the deposition of volatile compounds causing disastrous secondary changes. The ideal brick would be entirely free from iron impurities, have minimum permeability combined with sufficient resistance to internal fissuring, and be refractory enough to withstand possible overheating. The influence of dust in the regenerators is considered and suggests alteration in their construction to diminish the trouble due to it. Sir Robert Hadfield[43] describes experiments made with fireclay, magnesite, and plumbago for stoppers and nozzles for steel ladles. Good results were obtained with magnesite, especially with steels containing 0·90 % of manganese and upwards, which have a severe chemical action on fireclay nozzles. Plumbago was found to possess no advantages over fireclay. An excellent bibliography of the literature relating to refractories is appended to this paper, and analyses of a large number of English and foreign refractories and the raw materials from which they are produced are quoted.

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[39] *Trans. Amer. Ceram. Soc.*, 1916, **18**, 557.

[40] *Trans. Amer. Ceram. Soc.*, 1916, **18**, 524; *J.*, 1917, 714.

[41] *Trans. Amer. Ceram. Soc.*, 1916, **18**, 263.

[42] *Trans. Faraday Soc.*, 1917, **12**, 153. *Trans. Ceram. Soc.*, 1917, **16**, 71. *J., Iron and Steel Inst.*, 1916, **7**, 172; *J.*, 1917, 647.

[43] *Trans. Faraday Soc.*, 1917, **12**, 12; *J.*, 1916, 1218.

J. W. Mellor[44] deals with the texture of firebricks. An elegant method for observing the textures is described. The specimen is cut transversely and an exposed face polished. To this polished face a glass plate is then cemented by means of hot Canada balsam. The texture of a refractory may vary from that of the light porous bodies used in making insulating bricks to non-porous or vitreous bodies used in making acid-resisting brick for acid towers, etc. It is impossible to over-emphasize the importance of uniformity in texture, be it coarse or fine. Assuming that the chemical composition and refractoriness are satisfactory, the life and character of the brick are largely determined by its texture. If the vitrification of a clay is the result of reaction between the surfaces of contact of the granules, the speed of vitrification must increase when the area of the surfaces in contact with one another is augmented. It follows also that pressure might be expected to lower the softening temperature of a clay by bringing the surfaces of the granules into more intimate contact. Observations showed that with clays of approximately the same grain size,[45] the softening temperature is reduced by pressure in accord with the exponential law, softening temperature $= Ce^{kp}$ where C denotes the squatting temperature of the clay under no load, p denotes the pressure in lb. per sq. in., and k is a constant of the order 0·001, but which has in general smaller values for silicious than for aluminous clays. Anything which favours the vitrification of a clay reduces its refractoriness and consequently, other things being equal, the coarser the grain of a clay the higher its softening temperature, and the coarser the texture, the more refractory the brick. For example, firebricks made with some clays, with or without fine-grained silica, fail at temperatures which they withstand when made from the same clay mixed with coarse grained silica. The quartz fragments must be angular and not in the form of rounded pebbles. The changes which occur during the firing of refractory materials are called by this author *arrested reactions*, as the chemical and physical changes are arrested at the particular and definite stages before they are completed.

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[44] *Trans. Ceram. Soc.*, 1917, **16**, 40; *Trans. Faraday Soc.*, 1917, **12**, 53; *J.*, 1916, 1218.

[45] *Trans. Ceram. Soc.*, 1916, **15**, 117.

This explains why the true thermal expansion of fire bricks is difficult to measure[46] as it is obscured by secondary effects due to after-expansion or after-contraction.

W. G. Fearnsides[47] puts in a plea for the further application of petrographic methods to the study of refractories. C. H. Desch[48] adopts the method of grinding one surface only of the specimen in the usual manner for petrological work and examining in the etched or unetched condition by means of a metallographic microscope with a vertical illuminator. Sharp photographs of a eutectic structure in Portland cement clinker were obtained which was quite invisible in thin sections of the same clinker, owing to the elements of the structure being of less size than the thickness of the section. The different constituents can be distinguished by etching with dilute hydrofluoric acid or other reagent. Hancock[49] separated a typical Stourbridge fireclay into six fractions by elutriation. The chemical composition and rational analysis of the fractions and original clay indicated that the clay substance constituted the bulk of the finest fraction and that the quartz tends to accumulate in the coarser fractions.

R. B. Sosman[50] discusses the two and three component systems made from silica, alumina, magnesia, lime, and the oxides of iron. He concludes that the stable compounds of these oxides with each other consist of the oxides in simple proportions, usually 1 : 1 or 2 : 1, and that these compounds are molecular compounds of the oxides. The three-component systems fall under similar generalization, the ternary compounds being composed of the more stable binary compounds in simple proportions, usually 1 : 1. The maximum melting points in all the two and three component systems are the melting points of pure stable compounds, and the highest melting points of all are those of the pure oxides alumina, lime, and magnesia. Any finely powdered substance, if held slightly below its melting point, will sinter together more or less solidly and it is suggested that there is therefore no reason why a pure oxide, such as alumina, cannot be made into a dense, hard refractory without the aid of a bond. Phase rule diagrams of all the possible two and three component systems which can be made from the six oxides dealt with are given. It is suggested that kaolinite ($Al_2O_3,2SiO_2 2H_2O$) when heated breaks up into a mixture of Al_2SiO_5 and SiO_2. Mellor and Holdcroft[51] consider from experimental evidence that in the region of 500° C. kaolinite breaks up into free silica, free alumina, and water and that the Al_2SiO_5 (sillimanite) is formed at 1200° C. by the recombination of the free alumina with some of the free silica. Sokolov[52] heated Gluchov kaolinite for periods of 1 to 5 hours at temperatures from 200 to 1000° C., digested the residue for 2 hours with 16 % hydrochloric acid and determined the soluble alumina. The following results were obtained after ignition for 1 hour.

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[46] *Gas J.*, 1917, **138**, 502.

[47] *Trans. Faraday Soc.*, 1917, **12**, 64

[48] *Trans. Faraday Soc.*, 1917, **12**, 67.

[49] *J.*, 1917, 747.

[50] *Trans. Faraday Soc.*, 1917, **12**, 170. *J. Ind. and Eng. Chem.* 1916, **8**, 985; *J.*, 1917, 136.

	water lost %	Al_2O_3 soluble %
300° C.	... 0·73	... 2·12
400° C.	... 0·67	... 2·08
600 C.	... 10·49	... 28·46
700 C.	... 11·92	... 32·30
800 C.	... 12·99	... 34·66

A weak alkali extracts soluble silica from the residue. The results are taken as indicating that at 800° C. the kaolin molecule is completely broken down into its component oxides. The soluble alumina is much greater than was obtained by Mellor and Holdcroft, and if the experimental work is correct, strong support is given to the view of the latter workers as to the constitution of the kaolinite molecule, as there is no indication of the "dehydration" taking places in stages such as might occur if the elements of the "combined water" were placed unsymmetrically in the molecule. J. W. Mellor[53] has investigated the heating curves of crystalline kaolinite, fireclay, halloysite, silicic acid, allophane, and pyrophillite. Halloysite having no critical point at 500 C. is thus distinguishable from kaolinite. Allophane and other hydrated alumina-silica minerals give heating curves similar to halloysite. The conclusion is drawn that the dominant mineral in Glenboig, Lancashire, Stourbridge, and other fireclays and also in Devon and Dorset ball-clays is *clayite*, a colloidal form of kaolinite. Evidence is adduced for the presence of true kaolinite in ball-clays. W. G. Fearnsides[54] discussing the constitution of coke-oven bricks, agrees with the conclusion that at 1200° C. kaolin changes into a mixture of sillimanite and free silica (probably in the form of tridymite changing at higher temperatures into cristobalite). On cooling from higher temperatures an eutectic is formed with a melting point as determined by Rankin of 1600° C., and the conclusion is drawn that kaolin and quartz may therefore be mixed in any proportions with little loss to their refractoriness. It is unnecessary for the refractoriness of coke-oven bricks to be as high as that of bricks for steel furnaces.

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[51] *Collected Papers*, Vol 1, 1914

[52] *Kryst. Min.*, 1915, **55**, 195 ; *J*., 1917, 1177.

[53] *Trans. Ceram. Soc.*, 1916-17, **16**, 73 ; *J.*, 1917, 548.

[54] *Gas J.*, 1917, **137**, 253 ; *J.*, 1917, 216.

N. B. Davis[55] examined a number of firebricks which had during use become impregnated with copper sulphides, galena, and metallic zinc and zinc oxide. In a brick from the fore-hearth of a copper-blast furnace which had been in contact with the molten matter, the original coarse texture of the brick was almost completely destroyed. Polished surfaces showed the sulphide to be wholly present as chalcopyrite filling pore spaces in the altered brick.

As a means of preventing the disintegration of the surfaces of coke oven bricks, which are to be in contact with the coal, M. Barrett[56] proposes to glaze these surfaces immediately the bricks are made. During the burning, whilst the bricks are still incandescent and at a temperature of not less than 1200° C., they are treated for about 30 minutes with the vapours of alkaline chlorides. The parts not required to be treated may be coated with a wash of barium sulphate.

B. J. Allen[57] describes a new method of casting articles of fireclay. In the Weber process of casting, a slip (containing coarse and fine grog) obtained by the use of suitable flocculents, is poured into a mould with plaster faces. Allen's method is to surround the plaster mould with an iron case and maintain a vacuum between the mould and the casing, thus greatly increasing the filtering power of the mould and enabling a deposit of clay of any reasonable thickness to be obtained. The deposit is homogeneous and the vacuum is maintained until the article is hard and self-supporting. Variations in thickness of the article are obtained by varying the space between the case and the mould. Illustrations and descriptions are given of the adaptation of the method to the casting of open and covered glasshouse pots, condensing worms, and chemical ware. A combination of this suction process with a process of electro-deposition is also described. The apparatus consists of a metal case surrounding the mould and forming one electrode, the other electrode being a suspended perforated metal tube. The mould is kept full of slip, and on passing the current the material in suspension migrates to the mould and the water accumulates round the suspended tube and is siphoned off through insulatde pipes. When a deposit of sufficient thickness has been thus obtained the remaining slip is siphoned off and the deposit dried by suction. The density of the deposit depends on the voltage used. If a dense slip is used the plaster mould and suction have been found unnecessary, the simple metal mould being sufficient. Articles of plumbago and carborundum have been made by this method. The development of these casting methods will be followed with interest, as large economies of labour may result from them.

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[55] *Economic Geology*, 1917, **10**, 663.

[56] Eng. Pat. 103953, 1916; *J.*, 1917, 388.

[57] *Trans. Ceram. Soc.*, 1916 17, **16**, 134; *J.*, 1917, 549.

Silica Refractories.

Boswell[58] has surveyed our home resources of sands used in metallurgical practice. It is pointed out that in high-class moulding sands with natural bonds, coarse sand and clay grades predominate, other grades like fine sand and silt being subordinate. The clay yields the "glue" which holds the quartz grains together even at high emperatures. In the Bunter red sands of the Birmingham district the lay or mud grade which forms the bond is a thin coating of ferric oxide round each grain of quartz. This iron oxide holds a film of water by surface tension, thus making a strong bond between the quartz grains. It is important to note that some of the most successful steel moulding sands, such as the "Belgian Red" and "Yellow" and 'Cornish Red" (Pliocene deposits, St Erth) owe their colour to iron oxide and are associated with glauconite-bearing deposits. Colloidal silica may be in itself an important bond as well as the colloidal glauconites. The author considers that all foreign sands imported before 1914 can be replaced by home materials, although under the conditions then existing it might not in some cases be economical.

McDowell[59] deals with the composition and behaviour on heating of silica bricks. According to Wernicke and Wildschrey, good quartzites for silica brick-making consist of quartz grains in a ground mass or cement of amorphous silica, and owing to the slight sintering caused by fine fluxing impurities in the ground mass they are much stronger after burning than quartzites which have little ground mass or cement. Microscopic examination of American quartzites does not support this view. It is considered that in the first burn of silica bricks most of the quartz is converted into cristobalite, and on repeated burning the rest of the quartz is slowly transformed. The cristobalite inverts to tridymite, slowly at first, but more rapidly at later stages, time and burning temperature being the controlling factors. The author suggests that the catalytic action of the flux compounds formed with the added lime probably explains the observed inversion of cristobalite to tridymite, and that therefore an increased amount of lime in bricks should accelerate the formation of tridymite.

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[58] *J.*, 1917, 753. *Trans. Faraday Soc.*, 1917, **12**, 104.

[59] *Trans. Amer. Inst. Min. Eng.*, 1916, 1999. *Trans. Ceram. Soc.*, 1916–17 **16**, 52.

Le Chatelier[60] points out that the transformation of quartz into cristobalite and tridymite is accompanied by a recrystallization which gives to the bricks great solidity at high temperatures and by an expansion frequently very considerable. In 1912 he showed that Dinas bricks after firing, but before use, consisted largely of a variety of silica with a transformation point at 215 C. accompanied by a sharp change of linear dimension of 1 %. Accurate determination of the transformation temperature of cristobalite (230° C.) showed it to be identical with this variety referred to. The three varieties, tridymite, cristobalite, and vitreous silica, have about the same density of 2·20 at temperatures of 1000° C. Silica bricks from the arches of old furnaces contained crystals originally cristobalite which had been transformed into tridymite, forming a multitude of small crystals enclosed by the old crystals. In another case the bricks showed small crystals of cristobalite formed directly from quartz, the grains of which had been fluxed together at a temperature of about 1700° C. Crystallization of tridymite was also observed in the linings (consisting of a mixture of ganister and clay) of a Bessemer converter at Sheffield. It is apparent that in all cases rapid crystallizations of silica from a melted glass give cristobalite. The quartz grains directly transformed present no appearance of crystallization, and do not even act on polarized light, but the confused cristobalite can be identified by the roughly circular crevices giving the mass the appearance of an agglomeration of little spheres. Fenner showed that if a thin translucent splinter of a silica brick be heated above 230° C., its transparency will be seen to increase suddenly, due to the expansion bringing in contact the lips of these crevices. Cristobalite is more stable at elevated temperatures than quartz, but less so than tridymite, into which it tends gradually to transform. The conditions which promote the change from quartz to cristobalite, if prolonged, promote the change from cristobalite to tridymite. In the portions of silica bricks which in use have been for some weeks at a temperature over 1400° C., the transformation into tridymite is practically complete. According to Fenner's experiments, tridymite would only constitute the most stable phase up to 1480° C., and that between this temperature and the fusion point, 1780° C., cristobalite would be the stable phase; but Le Chatelier points out that this conclusion is in opposition to his observation that in steel furnaces when the temperature is much higher than 1480° C., silica bricks are completely transformed into tridymite. Fearnsides,[61] with regard to this, points out that when molten steel is run into a mould built up of quartz sand with an aluminous or ferruginous clay bond, the silica grains in the burnt skin of the mould, after the casting has cooled, are invariably found with a pellicle of cristobalite surrounding each cracked quartz grain, and this is quite in accord with the view of Le Chatelier, that after heatings of short duration followed by rapid cooling, cristobalite only is always observed. The surfaces of some silica bricks from the crown of a Martin furnace which were examined had been fused, which infers a temperature of 1750 to 1800 C. A photograph shows very clearly the limit of the melted part, and the crystals of tridymite formed before fusion are preserved unchanged by their contact with this, and they are consequently still stable at 1750° C Le Chatelier attempted to verify his conclusion that tridymite is the only variety of crystallized silica stable at high temperatures by heating to 1700° C. a small fragment of tridymite. There was no indication of change into cristobalite. The experiment is not regarded as decisive, as the temperature was maintained for two hours only. Fearnsides, in 1916,[62] attributed the quick-burning properties of true ganister to the presence of some small quantity of impurity which causes the change from quartz into tridymite to take place at comparatively low temperatures, and this is in accord with the view now advanced by Le Chatelier that tridymite is most readily formed from quartz by the intervention of some silicate flux or solvent in which the quartz is dissolved and out of which, when the solution becomes saturated with silica, the tridymite crystallizes Scott[63] has examined a number of silica bricks which had been for many months at a temperature over 1500° C. and found that the hottest parts of the brick were entirely tridymite, but cristobalite mixed with tridymite appeared some distance from the hot end, while towards the cool end there were partly converted quartz grains. This further confirms Le Chatelier's view as to the stability of tridymite. Scott found that in unused silica bricks most of the quartz is still unaltered and this is confirmed by observations made by Fearnsides Fenner[64] considers that the fact that tridymite is found in bricks which have been exposed to a temperature of over 1500° C is not contradictory of his conclusions but is consistent with the extraordinary sluggishness of inversion which he found to be a general feature of the silica minerals. Le Chatelier suggests that Fenner's[65] very exact experiments have been wrongly interpreted by their author. It is, however, evident that further carefully controlled experimental work is necessary before the question of the exact mechanism of the changes from one form of silica to another can be answered. Johns[66] points out that in a seasoned silica brick in an open-hearth steel furnace the exposed face is darker and denser, more refractory, and capable of withstanding temperature variations without fracture. From this dark portion, finely crushed, a magnet will remove up to 15% of magnetic oxide of iron which is the stable oxide at high temperatures, and does not combine with silica nor form a solid solution at high temperatures. In Japan a ferruginous quartzite containing 1·5% of finely disseminated ferric oxide made bricks more refractory and better capable of withstanding temperature changes than the usual silica bricks. It is, of course, only in an oxidizing atmosphere that the presence of magnetic oxide of iron in a silica brick can be an advantage. Le Chatelier and Bogitch[67] in determining the mechanical strength of silica bricks at high temperatures, obtained the following results on a "Star" (U.S.A.) silica brick:—

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[60] *Revue de Métallurgie*, 1917, **14**, 73; *J.*, 1917, 964.

[61] *Trans. Ceram. Soc.*, 1917-18, **17**, 20.

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[62] *Trans Inst Min Engineers*, **3**, 270
[63] *Trans Ceram. Soc*, 1917–18, **17**, 18
[64] *Trans Ceram Soc*, 1917–18, **17**, 30.
[65] *Amer J. Sci*, 1913, **36**, 331.

Temperature, °C.	Resistance to crushing, kilos per sq. cm	Temperature, °C	Resistance to crushing, kilos per sq. cm.
15	170	1200	85
520	158	1320	62
670	150	1460	50
800	139	1540	37
950	125	1600	30
1050	120		

Extrapolation to 1700° C. gives 12 kilos. per sq. cm. as the crushing strength which is about 10 times the pressure of the superincumbent brickwork in the crown of a steel furnace, so that the stability of the bricks in this position is assured.

Nesbitt and Bell[68] record experiments on the influence of pressure and fineness of grinding on the quality of silica bricks. The pressure in making the bricks was varied from 187 to 2500 lb. per sq. in. Tests on slag penetration, impact strength, and linear expansion indicated that little was gained by raising the pressure and obtaining a denser product. In tests on bricks made from materials ground to pass 12,- 8,- and 4-mesh sieves, the fine ground material gave the stronger bricks but the coarser material gave the greater resistance to spalling. The 4-mesh material pressed at 1500 lb. per sq. in. gave bricks which had the same spalling loss as handmade bricks and as they were better shaped and finished, power pressing instead of hand making is advocated. Le Chatelier and Bogitch[69] carried out experimental work which clearly indicates that the substitution of the impalpable powder obtained by grinding in a tube mill for the ordinary fine material considerably increases the mechanical resistance of the bricks at 1600° C.—one of the most important properties influencing durability. Test bricks were made using crude quartzite containing grains up to 4 mm. square, impalpable quartz powder, finely powdered quartz (sifted through a 100 sieve), with in each case 2 of lime. They were fired at Cone 19. Their results were. -

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[66] *Trans. Faraday Soc.*, 1917, **12**, 81.

[67] *Comptes Rend.*, 1917, **165**, 218 ; *J.*, 1917, 963.

[68] *Met. and Chem. Eng.*, 1917, **17**, 181 ; *J.*, 1917, 1049.

Composition of mixtures.	Linear expansion, %	Density.		Crushing strength in kilos per sq cm		
		Apparent.	Real	Cold		At 1600° C
				Dried	Burnt.	
75 Crude quartzite 25 Impalpable „ 2 Lime	5·2	1·63	2·35	15	165	30
75 Crude quartzite 25 Fine „ 2 Lime	—	—	2·33	10	60	8
25 Crude quartzite 75 Impalpable „ 2 Lime	3·9	1·36	2·35	9	135	10
25 Crude quartzite 75 Fine „ 2 Lime	—	—	2·33	6	52	3

The most suitable mixture was that containing 25 % of impalpable quartz powder and further trials with other quartzites confirmed this. These experimental results are confirmed by work carried out during 1916 and 1917 at the Dunes Works (France) by Philippon.[70] Test pieces were made with different varieties of French quartz and

[69] *Comptes Rend*, 1917, **165**, 742; *J.*, 1918, 8A

[70] *Comptes Rend.*, 1917, **165**, 1002; *J.*, 1918, 30A.

quartzites and with Pas de Calais sandstone. The conclusions drawn from the results obtained are (1) The crushing strength after drying and burning is proportional to the fineness of the quartz employed. (2) Different varieties of quartz were all equally capable of producing strong bricks if finely pulverized. (3) The expansion during burning is proportional to the size of the grains and is practically nil with bricks made with finely powdered quartz. (4) The strength after burning is fairly constant between 1 and 2 % of added lime, beyond which it decreases. As a result of these tests a formula was established for the production of the standard brick now manufactured at the Dune Works. Quartz, quartzites, or sandstone containing at least 96 % of silica is used. The proportion of lime is reduced to 0·6 % (*i.e.*, 2 % on the impalpable material) and 30 % of impalpable powder to 70 % of grains between 1 mm. and 8 mm. in diameter is used. The bricks are burned at 1300° C. in a tunnel kiln. The crushing strength (cold) is 200 to 250 kilos. per sq. cm. and the average expansion in burning is 1·6 %. The absolute density is about 2·4, the apparent density 1·9, and the fusing point about 1780° C. At present bricks of this make have lasted over 200 charges in the open-hearth steel furnace and are expected to stand over 300 charges. These important results should receive the attention of all silica brick manufacturers.

Magnesite Refractories.

Considerable trouble has been experienced in electric and other high temperature furnaces with spalling in magnesite bricks, and this has been more evident in machine-made than in hand-made bricks. It has been considered that this spalling was due to shrinkage with a corresponding increase in specific gravity. Well shrunk bricks with a sp. gr. of 3·7 are less prone to spalling as the change in volume on further heating is too small to set up serious strains. J. W. Mellor[71] considers that the remedies for spalling are to fire the bricks so as to secure the formation of a high proportion of β-magnesia and to keep the porosity of the bricks reasonably low. Le Chatelier and Bogitch[72] have examined the refractory properties of various magnesite bricks, and for purposes of comparison a chrome brick. 1. Styrian brick made in 1890. 2. Eubée brick made in 1910. 3. Brick of good present day manufacture. 4. Brick of medium quality made with the addition of 3 % of roasted iron pyrites. 5. Pure magnesite melted in the electric furnace. 6. Magnesite of brick No. 4 agglomerated in the electric furnace. 7. Chrome brick.

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[71] *Trans. Ceram Soc.*, 1916–17, **16**, 85; *J*, 1917, 551.
[72] *Comptes rend.*, 1917, **165**, 488; *J.*, 1917, 1236.

Chemical Analysis.

	1	2	3	4	5	6	7
MgO	86·7	93·4	89·4	81·2	93·7	88·5	12·3
CaO	1·0	3·7	4·5	4·8	2·7	4·5	5·8
Fe_2O_3	6·0	0·5	1·1	4·2	0·3	1·4	15·5*
Al_2O_3	0·6	0·2	0·8	1·0	1·1	0·0	10·9
SiO_2	6·7	2·8	4·2	8·8	3·2	6·5	4·7
Cr_2O_3	—	—		—		—	50·0
MnO	—	—	—	—	—	—	1·5
	101·0	100·6	100·0	100·0	101·0	100·9	100·7

* FeO

Crushing Strength in kilos. per sq. cm.

Temp	1	2	3	4	5	6	7
15° C	145	420	390	230		530	260
1000° C	85		—	—	—	—	120
1300° C	66		—	—			6
1500° C	3·6	185	790	16	790		2
1600° C	1·8	8	4·8	3·5	6·6	3·5	1

All magnesite bricks show this sudden fall in strength above 1300°C. in proportion to their purity. Apparently the impurities suddenly melt in such a way as to leave the grains of magnesia isolated in the molten magma and they are then like wet sand, and possess only feeble mechanical strength. The results indicate why magnesite bricks in furnace linings present less resistance than silica, although their fusion temperature at ordinary pressures may be much higher. The rate of loss of strength in the chrome brick is analogous to that of the magnesite except that the rapid loss begins at 1100° C. instead of 1300° C.

Gosrow[73] has used electric furnace shrunk magnesite ground to pass a 6-mesh sieve and mixed with 13 % of powdered (80-mesh) ferric oxide, 5 % of basic steel furnace slag, and 12 % of well boiled tar. The mixture was rammed round a steel plate so as to make the lining of a Stassano furnace in one piece in position. Brooke[74] considers that the Styrian magnesite bricks owe their value to fine grinding, high preliminary burning, powerful hydraulic pressure in making, and final burning at high temperature so as to secure the formation of β-magnesia.

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[73] *Met. and Chem. Eng.*, 1917, **17**, 416 ; *J.*, 1917, 1236.

[74] *Trans. Ceram. Soc.*, 1916-17, **16**, 205 ; *J.*, 1917, 1273.

Zirconia.

Audley[75] usefully sums up the occurrence, properties, and applications of zirconia. An account is given of the chief results obtained by Ruff and Lauschke, and tables are given showing the melting temperatures and contraction of mixtures of zirconia with other oxides. Dense objects with a zirconia basis suitable for use in exhausted carbon-resistance furnaces with reducing atmospheres can be burned in these furnaces at temperatures over 2000° C. Suitable additions to the zirconia are:—for burning at 2000° C., about 1 % of alumina; at 2200° C., about 1 % of thoria; at 2400° C., about 1 to 3 % of yttria.

Podszus[76] has obtained good results in the manufacture of articles of pure zirconia by first of all fusing the zirconia by embedding a carbon electrode in coarsely ground, calcined zirconia and heating this by the arc formed from a second carbon electrode. The zirconia is thus partially melted with the formation of some carbide which then acts as an electrode; after a time the arc becomes quiet and fusion proceeds rapidly. The fused zirconia, which has a hardness between quartz and corundum, a sp. gr. of 5·89 and melting point about 3000° C., is then ground in a steel ball mill (any iron taken up being removed by subsequent treatment with hydrochloric acid) and moulded or pressed with or without the use of an organic bond. By reducing a portion of the zirconia to the colloidal form the material can be rendered plastic and the process of slip-casting used. The articles are burnt at 2300°–2400° C. in a furnace of the injector type constructed mainly of fused zirconia and heated with coal gas, petroleum, or acetylene and compressed oxygen.

Rosenhain[77] has purified crude zirconia by washing with dilute sulphuric acid; the iron oxide was reduced from 3·5 to 1·5 % with a consequent improvement of the refractoriness.

Meyer[78] refers to the use of zirconia as a surfacing material for silica, bauxite, or other refractories. It is stated that a thin layer of zirconia with a suitable binder renders the coated article highly resistant to slag corrosion.

Bauxite.

A. de Keppen[79] divides the French bauxites into three classes. 1. Bauxites with 60 % Al_2O_3, under 4 % Fe_2O_3, and only traces of silica, used by chemical works. 2. Red bauxites with 60 % Al_2O_3 and 3 % SiO_2 for aluminium manufacture. 3. White bauxites with 45 % Al_2O_3, traces of iron and much silica, for refractories. Average analyses of Var bauxite (nearly half the world's supply) are –

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[75] *Trans. Ceram. Soc.*, 1917, **16**, 121; *J.*, 1917, 551.

[76] *Z. angew. Chemie*, 1917, **30**, 17; *J.*, 1917, 217.

[77] *Trans. Faraday Soc.*, 1917, **12**, 96.

[78] *Brick and Pot. Lr. J.*, 1987, **55**, 121.

[79] *Trans. Ceram. Soc.*, 1917, **16**, 32.

	White bauxite	Red bauxite
Alumina	58 to 64	50 to 65
Iron oxide	4 to 8	12 to 25
Silica	7 to 10	1 to 3

Certain varieties contain up to 35 % of SiO_2.

CERAMICS.

In Russian Poland and South Western Russia a good deal of earthenware is made from a body containing limestone as one of its ingredients, and it is suggested by Teichfeld[80] that this class of cheap ware should be produced in this country. The finished ware is about 10 % lighter than English earthenware. Binns and Blumenthal[81] have experimented with American raw materials for the production of china. The formula used was kaolin 27, ball clay 15, flint 36, felspar 19·5, whiting 1.5, magnesium carbonate 1. Kaolin from various sources was used, but the other ingredients were from the same source in all the trials Their results indicate the possibility of producing from American materials, chinas which in appearance are equal to those made from English materials. The American kaolins required rather more to make a casting slip than the English. The colour of the trials burned at cone 10 was better than those burned at cone 9

B. Moore and J. W. Mellor[82] have reviewed the work of Seger, Sosman and Merrom, Brougniant, Jackson and Hopwood, Orton, and others on the discolorations occurring in the manufacture of pottery and bricks. They conclude that the reddening of buff and white clays is due to the formation on heating of free ferric oxide, alumina, and silica which at a later stage react with the fluxes present forming under reducing conditions bluish-gray or pale green colours and under oxidising conditions a pale yellow colour.

It is suggested that blue or brown discolorations in bone china are due to the formation of ferrous phosphate and that a brown discoloration may be due to the formation of ferric chloride which is later oxidised to red ferric oxide. Keane[83] attributes the yellow colour of bricks to ferric oxide in a very finely divided state and uncombined with lime or silica. Ferric oxide in a coarser condition gives a red colour to bricks. Alumina is considered to be of special importance in bricks which have a yellow colour when the ratio of free alumina to iron oxide is high and it is suggested that lime acts indirectly by setting free alumina. Anhydrous yellow ferric oxide has not been isolated, but it is stabilised by other substances. Thus the buff coloration produced when aluminium hydroxide containing a small quantity of ferrous hydroxide is ignited is undoubtedly due to ferric oxide, as is also the yellow colour of slightly impure quicklime. Clay associated with organic matter and therefore likely to contain oxide of iron in a fine state of division may burn to a buff colour without the lime or alumina content being high. As agglomeration increases with temperature yellow bricks might be expected to turn red if heated sufficiently, but on the contrary red bricks become paler or even buff when re-heated, and it is considered that this is due to the "peptising" action of alumina increasing to such an extent with the temperature as to render it the predominating factor.

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[80] *Trans. Ceram. Soc.*, 1916-17, **16**, 1 ; *J.*, 1917, 549.

[81] *Trans. Amer. Ceram. Soc.*, 1916, **18**, 619.

[82] *Trans. Ceram. Soc.*, 1916-17, **16**, 58 ; *J.*, 1917, 556.

[83] *J. Phys. Chem.*, 1916, **20**, 734 ; *J.*, 1917, 138.

Klein[84] considered that needles of sillimanite are formed in pottery bodies only to a slight extent between 1250 and 1275° C. and not at all at lower temperatures, being formed in abundance only above 1300° C. He consequently claimed that it was possible to estimate the burning temperature of porcelain bodies from the development of sillimanite crystals in them, and that the duration of burning is less important than the temperature. This view is criticised by J. W. Mellor[85] who points out that Heath and Mellor in 1907[86] showed that sillimanite crystals can develop abundantly in bodies which have never reached 1200° C. and that they develop more freely in particular mixtures. Mellor considers that sillimanite developments can be obtained by long firing at a lower temperature similar to those obtained at a higher temperature.

Bleininger[87] reviews the composition and behaviour of porcelains. He divides them into the following types: 1. American; 2. Hard fire (Austria, Denmark, France, Germany, Japan, and Sweden); 3. Soft (early French, Japanese, and Seger porcelain), 4. Bone China; 5. Parian; 6. Refractory and special.

American type porcelain is distinguished from European hard fire porcelain by the lower glazing temperature of the second firing after the body has been matured by the first firing. Refractory and special porcelains include the well-known Marquardt body, in which by the addition of alumina to kaolin the composition of sillimanite is obtained. The minimum amount of felspar to give sufficient vitrification is used. Diagrams showing the relations between the porosity, contraction, and temperature are valuable in indicating the proper vitrification temperature and the point of overfiring resulting in the formation of a vesicular spongy structure. Addition of quartz reduces the drying shrinkage and prevents warping, and in firing it forms the skeleton of the body, increasing its rigidity and preventing deformation. The solution of quartz in felspar apparently commences at about 1325° C., it is marked at 1375° C., and above 1425° C. practically no quartz grains remain undissolved. No indication of the transformation of quartz to tridymite or cristobalite has been observed, which Klein suggests may be due to solution taking place more rapidly than transformation to other crystalline forms. Quartz previously calcined appears to give better results than the raw ground material. The mechanical strength, thermal, electrical, and chemical properties of porcelain are discussed. It is observed that the resistance of chemical porcelain to sudden heating and cooling is usually determined by heating the specimen to redness and either cooling it rapidly in a current of cold air or quenching it in water, and it is suggested that the more systematic procedure would be to heat specimens to a definite temperature and to quench them suddenly in water, noting the number of such treatments they can withstand. 200° C. is suggested as a suitable temperature, or a series of tests commencing at 150° C. and rising by steps of 10° C.

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[84] *U.S. Bureau of Standards, Tech. Paper* 80; *J.*, 1916, 1220.

[85] *Trans. Ceram. Soc.*, 1916-17, **16**, 71; *J.*, 1917, 550

[86] *J.*, 1909, 474.

[87] *Met. and Chem. Eng.*, 1917, **16**, 589; *Trans. Ceram. Soc.*, 1916-17, **12**, 78.

Klein[88] has investigated the micropetrographic characters of the clay, felspar-quartz, felspar-clay, and felspar-quartz-clay bodies burned at known temperatures, and also of commercial bodies of various grades from white ware to hard fired porcelain. Among the conclusions reached is that in quartz-clay-felspar bodies, at 1310° C., the felspar is present as a glass and the clay is almost completely dissociated with the formation of chiefly amorphous sillimanite (but little crystallized sillimanite), the quartz remaining undissolved. At 1380–1400° C. little quartz remains dissolved, and the sillimanite is in the crystalline form. Montgomery and Babcock[89] describe deformation and rapid heating and cooling tests. In both tests the European porcelains were found to be superior to American. It is suggested that a chemical porcelain should not deform below cone 25 and should be fired to cone 16, at which temperature the glaze should mature. An experimental body made from 80 clay, 10 flint, and 10 felspar was found to be as satisfactory under test as Royal Berlin.

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[88] *Trans. Amer. Ceram. Soc.*, 1916, **18**, 377; *J.*, 1916, 1220.

[89] *Trans. Amer. Ceram. Soc.*, 1916, **18**, 88; *J.*, 1917, 715.

Hertwig[90] maintains that good porcelain for vessels can be produced at cone 8 or even at cone 7. In three cases porcelain with 30 % felspar addition developed numerous blisters on the glaze; this defect was traced to the use of a coal which slagged, and it was avoided by the addition of a little chalk to the body and the introduction of a larger quantity of pitchers into the glaze. Howat[91] gives the analysis of a Marquardt pyrometer protection tube as SiO_2, 35·12; Al_2O_3, 63·20; and K_2O, 1·65 %. A body of this composition has been prepared in the Bureau of Standards laboratory and tubes made from it are giving satisfactory results. Above 1350° C. the glaze is apt to stick, but improved glazes were under test. At 1450° C. the resistance to deformation is equal to that of the Marquardt tubes and the general resistance to temperature changes is equal to that of the imported tubes. Watkin[92] places the properties required in chemical porcelain in the following order of importance: — (1) Resistance to sudden changes of temperature; (2) resistance of the glaze to the action of chemical reagents; (3) the fusing point of the glaze should be well above the maximum temperature at which the articles are generally used. An account of the manufacturing processes is given and reference is made to the German and English methods of testing the finished ware. The opinion was expressed that there is now no serious need to go abroad for any chemical porcelain apparatus and the indications are that porcelain of home production, superior to the German makes, will soon be available. Howat[93] has studied the softening points of steatite—potash felspar. Mixtures of steatite and Maine or microcline felspar were made into small cones and rapidly heated in an electric furnace to 800° C. and then at the rate of 2·5° C. per minute until they deformed. It was found that with either felspar the eutectic contained 17 %–23 % of steatite.

Wunder[94] describes a method used to combine casting, the bringing up of the under-glaze, and the glazing in one operation, so that the object from the mould, as soon as it is air dry, can at once be set for glost firing. The mould is first filled with glaze, emptied again immediately, filled in with suitable thinly mixed under-glaze colour, again emptied, and finally the mould is filled with the casting slip. After the desired thickness is obtained, if the object is also to be glazed inside, the mould is emptied once more and immediately filled with glaze again. By this method, also, compound porcelain bodies have been made which endure several heatings and sprinklings with cold water, and in their resistance to abrupt temperature changes appear superior to the best German porcelain, although the compound layers consist of low-softening masses.

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[90] *Sprechsaal*, 1917, **50**, 152.

[91] *Trans Amer Ceram. Soc.*, 1916, **18**, 268; *J*, 1917, 715.

[92] *J.*, 1917, 749

[93] *Trans. Amer. Ceram. Soc*, 1916, **18**, 488; *J.*, 1917, 714

[94] *Sprechsaal*, 1917, **50**, 119; *Trans. Ceram Soc*, 1916–17, **12**, 99.

Kirkpatrick[95] has investigated the systems felspar-calcite and felspar-magnesite. He concludes that the system orthoclase-calcite has one well-defined deformation point maximum with 27·5 % calcite and two well-defined deformation-point eutectics with 3 % and 50 % calcite. The system orthoclase-magnesite shows one eutectic point at 3 % magnesite. The system albite-calcite has a long eutectic range from 10 % to 55 % calcite, and the system albite-magnesite also has a long eutectic range at from 5 to 20 % magnesite. The lowest fusion point with calcite mixtures occurs at cone 01 with 25 % calcite and 75 % albite, and with magnesite mixtures at cone 1 with 15 % magnesite and 85 % albite. The results tend to indicate that felspars are decomposed by calcite but not by magnesite. It is suggested that the best types of Bristol glazes lie in eutectic areas of the orthoclase-calcite system. Watts[96] has studied Bristol glazes compounded on the "*norm*" basis. Two series, each containing 45 mixtures, were prepared of the felspar-willemite-wollastonite series and the felspar-willemite-anorthite series. The glazes of Series I do not opacify if 0·5 or higher equivalent of felspar is present or unless the willemite exceeds 0·25 equivalent. At cone 4 the mixtures approaching the ternary eutectic have a brilliant gloss and towards the willemite end of the triaxial diagram a satin-like texture is developed; the other mixtures are matt or pinholed. In glazes of Series II mixtures containing less than 0·25 CaO or more than 0·25 ZnO tend to be opaque. Crazing only occurs with mixtures containing above 0·5 felspar or less than 0·25 CaO. All the glazes in this series are matt. The general evidence obtained indicates that (1) the temperature of maturity of a glaze is considerably lower if the lime is present as wollastonite norm than if present as anorthite norm; (2) the presence of anorthite norm tends to produce slips while the presence of wollastonite norm tends to produce glasses. The presence of willemite norm materially lowers the temperature of maturity of the glaze from that obtained by either felspar-wollastonite or felspar-anorthite mixtures; (3) a low felspar content is necessary to avoid crazing and more than 0·25 equivalent willemite norm must be present to make the glazes glossy. The same author[97] has studied Bristol glazes compounded on the eutectic basis. The most fusible mixture of modern Bristol glaze type was found to be obtained by mixing Canadian felspar 59·62, whiting 8·03, zinc oxide 6·50, Florida kaolin 13·81, and flint 12·04%, corresponding to (0·4 KNaO, 0·3 CaO, 0·3 ZnO) 0·60 Al_2O_3, 3·55 SiO_2. It deformed at cone 03. Glazes were made of this and allied mixtures and burned at cone 03–01 and cone 4 and it was found that there is a rapid increase of glossiness with a slight increase of felspar, greater white opacity with more ZnO, and a greater cream opacity with more CaO. Hill[98] has examined the results of Purdy's experiments on the effect of clay on the fusibility of Bristol glazes.[99] As these experiments left some doubt as to the amount of clay required for different proportions of CaO and ZnO to form a fusible glaze, a series of glazes to cover additions of clay between those used in Purdy's two series was planned. With an Al_2O_3 : SiO_2 ratio of 1 : 6 and CaO : ZnO of 3 : 1 any addition of clay up to 0·3 equivalent was found to render the glaze more fusible and Purdy's results were confirmed, but with CaO : ZnO = 1 : 1, clay was found to increase the fusibility up to 0·02 equivalent and further additions to decrease it. Glazes containing 0·30 equivalent of clay were found to be more refractory than those containing less clay or none, although according to Purdy's results this equivalent of clay is present in the most fusible glaze of its type. Within the limits studied, the most fusible glazes were those with a CaO : ZnO ratio of 3 : 1 and an increase of either base reduced the fusibility. It is suggested that if Purdy had added silica instead of clay to his earlier series of glazes the fusibility would have been increased and that the fusing point of these glazes would have been higher if clay alone instead of a mixture of clay and flint had been used. Parmalee and Williams,[100] investigating fritted leadless glazes for sanitary ware, found that for burning at cone 7 the best range of RO in the glaze was within the following limits :—0·1–0·6 K_2O, 0–0·3 ZnO, and 0·1–0·6 CaO, the other oxides being 0·5–0·6 Al_2O_3, 5 SiO_2, 0·5 B_2O_3. The glazes higher in lime were dull and those with more than 0·3 ZnO were liable to blister. The use of soda in place of part of the potash increased the range within which good glazes could be obtained. Glazes within the limits mentioned do not craze but become opalescent with an excess of alkali or boric acid. The most satisfactory glaze obtained was composed of :—*Frit* : nitre 1212, whiting 400, boric acid 1860, and flint 2520 ; *Mill batch* : frit 1450, whiting 366, felspar 1671, Florida clay 516, and flint 240. Keeler[101] has shown that for ordinary terra-cotta glazes the following limits are safe:—0·2–0·4 KNaO, 0·1–0·6 CaO, 0·1–0·4 ZnO, 0·02–0·1 MgO, 0·02–0·3 BaO, 0–0·6 PbO, 0·2–0·5 Al_2O_3, 1·5–4 SiO_2, and 0·02–0·15 SnO_2. High alumina and low silica tended to produce immature glazes with a tendency to flow and to craze when fused. Low alumina and low silica induced crazing, pinholes, and immaturity, and the stannic oxide was not dissolved. High silica and alumina produced beading, immaturity, and waviness but crazing was not observed. Low alumina and high silica gave fairly bright glazes showing waviness and becoming rougher with an increase in alumina. For good matt glazes it was found desirable to use a hard felspar and a mixture containing at least 0·35 K_2O, less than 0·35 ZnO, and low CaO. For clear glazes 0·3 K_2O, 0·3 CaO, 0·3 ZnO, 0·05 BaO, and 0·05 MgO gave good results at cone 4.

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[95] *Trans. Amer. Ceram. Soc.*, 1916, **18**, 575; *J.*, 1917, 714.

[96] *Trans. Amer. Ceram. Soc.*, 1916, **18**, 424; *J.*, 1917, 716.

[97] *Trans. Amer. Ceram. Soc.*, 1916, **18**, 631; *J.*, 1917, 716.

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[98] *Trans. Amer. Ceram. Soc.*, 1916, **18**, 508 ; *J.*, 1917, 716.

[99] *J.*, 1903, 1047.

[100] *Trans. Amer. Ceram. Soc.*, 1916, **18**, 812 ; *J.*, 1917, 717.

[101] *Trans. Amer. Ceram. Soc.*, 1916, **18**, 282 ; *J.*, 1917, 716.

Pukall[102] and Berdel[103] have investigated the most suitable formulæ for earthenware glazes without boric acid. As an example the latter worker gives 0·2 K_2O, 0·1 Na_2O, 0·1 ZnO, 0·1 MgO, 0·5 BaO, 0·16 Al_2O_3, 1·52 SiO_2, the frit for which is made from felspar 559, anhydrous pearl ash 138, calcined soda ash 106, zinc oxide 82, magnesite 84, barium carbonate 978, quartz 480. For the mill 155 parts of Zettlitz kaolin is added to 2080 of the frit.

Mellor[104] found that when a certain alkali lime boric frit was heated in the usual manner it developed blisters. These were found to be due to 5·41 % of water which entered into combination on grinding the frit in a wet state. When dry ground this frit gave no trouble. B. Moore had previously noticed the phenomena with other frits containing alkali.

ENAMELS

Kirkpatrick, Arnold, and Geiger[105] have endeavoured to apply an enamel coating to a stiff plastic column of clay extruded through a die, the column being afterwards cut into bricks. It was found that the addition to the enamel of 1 % of starch or 0·3–0·5 % of gum tragacanth gave the desired range of fit to bodies of varying composition and shrinkage. Promising results were also obtained by the addition of sodium silicate and oxalic acid to the enamels. Danielsen[106] has investigated the effects of variation in the composition of ground coats for sheet-iron enamels. In an enamel corresponding to 0·25 K_2O, 0·5 Na_2O, 0·25 CaO, 0·15 Al_2O_3, 2·0 SiO_2 0·5 B_2O_3, 0·25 F, part of the first three oxides was replaced by 0·01–0·04 CoO, or by 0·01–0·05 NiO, or by 0·02–0·114 MnO_2, or by equivalent mixtures of these oxides. The series gave good results as regards toughness but did not make a good smooth ground coat when flint was added to the enamel batch. The best ground coats were obtained with a mixture containing 0·4 CoO and 0·75 NiO which was heated on the steel until the enamel turned black. White grounds are considered to be not certain enough for commercial practice and the use of cobalt and nickel is advocated for the production of good coats. Eyer[107] produces antimonates of alkaline earths, aluminium, magnesium, zinc, tin, zirconium, beryllium, etc., for use as clouding agents for enamels by heating a mixture of antimony oxide and a metal oxide with ammonium nitrate until all the latter is driven off. Borate of lime minerals such as borocalcite or colemanite may be used for the production of enamels for iron[108] if they have been previously melted with a relatively large quantity of glass. The glass employed preferably contains a high percentage of alkali and may also contain boron, lead, or fluorine compounds.

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[102] *Brick and Pottery Tr. J.*, 1917, **25**, 107; *Sprechsaal*, 1917, 17, 25, 41, 59, 88; *Trans. Ceram. Soc.*, 1916–17, **12**, 108.

[103] *Sprechsaal*, 1917, 50, 72, 104; *Trans. Ceram. Soc.*, **12**, 1916, 109.

[104] *Trans. Ceram. Soc.*, 1916–17, **16**, 67; *J.*, 1917, 549.

[105] *Trans. Amer. Ceram. Soc.*, 1916, **18**, 139; *J.*, 1917, 717.

[106] *Trans. Amer. Ceram. Soc.*, 1916, **18**, 343; *J.*, 1917, 717. See also Eng. Pat. 107392, 1916; *J.*, 1917, 963.

As an opacifier for enamels the use of zirconium borate supersaturated with zirconia (*e.g.*, $ZrO_2, 2B_2O_3 + 4ZrO_2$) is suggested.[109] The materials are fused with cryolite or other alkali fluoride. It is claimed that this material has a much greater covering power than ordinary zirconium borate and does not cause the enamels to become spotty and dull. Mayer and Havas[110] prepare an opaque white enamel by adding a mixture of titanic oxide and zirconium oxide to the enamelling material.

KILNS.

L. B. Barringer[111] describes an efficient continuous kiln for the burning of porcelain. It consists of a straight tunnel, 197 feet long with a firing zone (1300°–1400° C.) rather nearer the discharge end. The combustion takes place in a chamber separated from the main tunnel by a narrow wall, and the air is preheated by being drawn from the discharge end through the goods which have passed on cars through the firing zone. The hot gases pass from the combustion chamber into the main tunnel through tuyères and a portion of the preheated air is deflected into the chamber to complete combustion. The products of combustion then pass towards the entrance and heat the incoming goods. The temperature of the gases leaving the tunnel is about 200° C. No details are given as to the fuel consumption in relation to the weight of goods fired.

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[107] Eng. Pat. 11083, 1915; *J.*, 1916, 839.
[108] Eng. Pat 101802, *J.*, 1917, 388.
[109] Eng. Pat. 101221; *J.*, 1917, 291.
[110] U.S. Pat. 1220253, 1917; *J.*, 1917, 504
[111] *Met and Chem Eng.*, 1917, **16.** 433; *J.*, 1917, 550.

In the improved Dressler kiln the weight of coal used is only 6 % of that of the clay goods burned at 1000° C. and 8 % when burned at 1200° C.

S. T. Wilson[112] has dealt with the firing of pottery ovens mainly from the point of view of fuel consumption, indicating the sources of waste. It is considered by this author that while continuous regenerative ovens may be economically used for burning firebricks and for high temperature ware which is not damaged by the action of combustible gases impinging on them, they cannot possibly be used successfully for china or earthenware.

BUILDING MATERIALS.

Bricks.

Burchartz,[113] from a grouping of all the types of bricks tested at the Materialprufungsamt between 1907–1913, proposes the following specification for clinker bricks, hard-burnt building ware, and best building bricks:—

--	Clinker brick	Hard-burnt ware	Best building bricks
Volume weight in grms per c c (r)	1·85	1·75	1·60
Specific gravity (s)	2·6–2·7	2·6–2·7	2·6–2·75
Impermeability $1 - \frac{r}{s}$	0·29–0·32	0·33–0·36	0·39–0·42
Crushing resistance in kilos per sq cm.	350	250	150

The loss in strength when saturated with water should not exceed 15 %, and after freezing should not exceed 25 %. The bricks should be free from lime in lump form and finely divided lime should be present in small quantities only.

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[112] *Trans. Ceram. Soc.*, 1916–17, **12**, 304; *J.*, 1917, 1273.
[113] *Mitt. k. Materialprufg.*, 1916, **34**, 79; *J.*, 1917, 597.

Dr. Boehme, of Berlin,[114] has made a series of tests, using cubes of brickwork 10 in. by 10 in. by 9·5 in., and found that the composition of the mortar has a marked influence on the strength which a wall will develop. One series of bricks used had a crushing strength of 263 tons per sq. in. With mortar composed of 1 part of lime to 2 of sand, the cube crushed under only 116 tons per sq. in., or 44 % of the crushing load of the individual bricks. With mortar composed of 1 of lime to 1 of cement to 6 of sand, the strength was 48 %, with 1 of cement to 6 of sand it was 55 %, and with 1 of cement to 3 of sand it was 63 %. In tests carried out at Toronto, pieces 9 in. square in section by 24 in. high had from 12 % to 29 % of the strength of the single bricks when laid in lime mortar, and 26 % to 61 % when laid in cement mortar. With piers tested at Watertown 24 in. to 120 in. high the ratio was from 11 % to 26 % for lime mortar. The Institute of British Architects tested piers 18 in. by 72 in. high and found strengths of 13 % to 22 % for lime and 17·5 % to 47 % for cement mortar. The tests indicate that the strength of brickwork is greater in small volumes than in larger, and that mortar containing cement gives better results than mortar containing lime.

Diamour[115] has examined sand-lime bricks with a view to determining whether they will endure the prolonged effect of heat such as they would be exposed to in the foundations or outer walls of furnaces and whether they are sufficiently resistant to the action of hot fumes to warrant their employment in the flues, chimneys, and walls of furnaces The tests were made on bricks containing 78·1 % silica, 14·1 % lime, and 6·8 % water and carbonic acid, and it is concluded from the results that these bricks are quite unsuitable for such purposes. Johns[116] has, however, successfully used Midhurst sand-lime bricks as an open-hearth steel furnace lining. These bricks were made from carefully selected and well-graded silica sand, sufficient lime being added to form a bond of hydrous lime silicate (probably $CaSiO_3,H_2O$) when subjected to high steam pressure for some hours in an autoclave.

Emley[117] gives a detailed account of the manufacture of sand-lime bricks and discusses tests for crushing strength, transverse strength, and absorption of water, and also freezing tests and fire tests.

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[114] Engineering Notes, *Daily Telegraph*, Sept. 24, 1917.

[115] *Revue de Métallurgie*, 1914, **11**, 203.

[116] *J. Soc. Glass Tech.*, 1917, **1**, 139.

[117] *Bureau of Standards*, *Tech. Paper* No. 85, 1917.

Cements and Concrete.

Campbell[118] has carried a step further his investigation on the constancy of volume of Portland cement. From an examination of some of the test bars for periods extending in some cases to 14 years the previous conclusions as to the injurious effect of free magnesia are confirmed. The effect on volume change of fineness of division of the cement was investigated and the conclusion drawn that with a finely divided cement expansion is much less than with a coarser cement of similar basicity. The same author, discussing[119] the conclusion of Le Chatelier that the two essential constituents of Portland cement are tricalcium silicate and tricalcium aluminate, finds that free lime is always present in cements prepared according to Le Chatelier's formulæ, as is also the case with cements made in accordance with the formula of Newberry, who concluded that the essential constituents are dicalcium aluminate and tricalcium silicate. Experiments are described which support the view that tricalcium aluminate is to be regarded as either a saturated solid solution of CaO in $5CaO,3Al_2O_3$, or as $5CaO,3Al_2O_3$ with four molecules of CaO of crystallization, rather than as a definite phase stable at all temperatures up to 1535° C.

Nitzsche[120] has compared the behaviour of Portland cement and blast furnace slag cements in water containing 1 % to 1·5 % of sulphuric acid, and concludes that although the acid solutions used were stronger than those likely to come in contact with concrete under ordinary conditions, the tests show that the blast furnace slag cements have the greater resistance to acids.

Abrams[121] has found that the rate of application of load has an important influence on the compressive strength of concrete. A machine speed giving a shortening of the test piece of 0·01 to 0·02 inch per minute per foot of length is recommended as a standard rate for compression tests. Edwards[122] has investigated the influence of the grading of sands and consistency of mix on the strength of plain and reinforced concrete. The results do not indicate any definite relation between the compressive strengths of 1 : 3 mortar cubes and of the concretes produced from the same sands.

Kitts[123] discusses the economical proportions for Portland cement mortars and concretes. Billings[124] gives an account of a specially made high-silica Portland cement used in the construction of a large concrete dam in Spain. The high-silica cement resists disintegration from exposure to the action of gypsum, alkali, and sea water, where high-alumina cements suffer serious damage.

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[118] *J. Ind. Eng. Chem.*, 1916, **8**, 1101; *J.*, 1917, 33.

[119] *J. Ind. Eng. Chem.*, 1917, **9**, 943; *J.*, 1917, 1236.

[120] *Armierter Beton*, 1916, **9**, 167; *J.*, 1917, 491.

[121] *Amer. Soc. for Testing Materials*, 1917.

[122] *Ibid.*, 1917.

[123] *Ibid.*, 1917. [124] *Ibid.*, 1917.

The use of concrete has proved unsatisfactory in some of the arid regions of the United States in which the soil contains free alkalis.[125] It is suggested that in such regions only a dense concrete made with not less than 1 part of Portland cement to 3 of aggregate with a minimum quantity of water should be used. The disintegration of porous concrete is due to the expansion of crystalline salts absorbed from the soil, and this absorption is not prevented by tar coating or cement grouting.

Harrison[126] traced the cracking of numerous structures of reinforced concrete in the Philippines to the presence of sodium chloride in the concrete mixture or in the water for wetting down the freshly set material. The failures appeared to be due to the bursting action of iron oxide formed in continuously increasing quantity around the embedded metal by the alternate formation and decomposition of ferric chloride.

Jackson[127] has studied the effect of grading the aggregate on the hardness and toughness of Portland cement concrete road-making materials. The results of his experiments indicate that in road construction greater resistance to wear would be obtained by increasing the coarse sand over the usual practice.

Hart[128] describes a useful method for the approximate determination of the proportions of sand and cement in hardened concrete.

Reeve and Lewis[129] consider that the difference in behaviour of various types of rock used in bituminous concrete road construction is due to differences in the surface character of the rock particles, the glassy surfaces of some particles failing to hold the bitumen so well as the rougher surfaces of others. It is considered possible by laboratory hardness and toughness tests of the aggregate to predict their relative behaviour in service.

Timber.

Rose and Lisse,[130] in an investigation on the decay of Douglas firs, obtained results indicating that the lignin is more resistant to decay than the cellulose, but does not appear to decay uniformly, the portion first attacked being that which yields acetic acid and furfural on hydrolysis, and the more resistant that which yields methylfurfural on treatment with strong hydrochloric acid, and methyl iodide when treated with strong hydriodic acid.

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[125] *U S. Bureau of Standards, Tech. Paper* 95

[126] *Eng and Min J*, 1916, **102**, 1019, *J*, 1917, 86

[127] *J. Agric Res*, 1917, **10**, 263; *J.*, 1917, 263.

[128] *Chem. Zeit*, 1916, **40**, 1032; *J*, 1917, 85.

[129] *J. Agric Res*, 1917, **10**, 319.

[130] *J. Ind Eng Chem*, 1917, **9**. 284; *J*, 1917, 457.

The Carbo-Teredo process has been found effective in Australia[131] in preserving wood against *Sphaeroma gigantea* and other borers prevalent in Australian harbour works and on land against the attack of white ants

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[131] *Engineering*, 1917, **103**, 174, *J.*, 1915, 1056, 1917, 388.

METALLURGY OF IRON AND STEEL.

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During the two years under review there have been no far-reaching developments in general practice, but much progress has been made in minor improvements, such as in the preparation and handling of materials, in the construction and equipment of furnaces, and in the recovery and use of by-products. There has, however, been very considerable development in the number and variety of electric furnaces used for making steel, and this subject is dealt with under the section on Electrochemistry (p. 276).

BLAST FURNACE AND FOUNDRY PRACTICE.

The charging of materials into blast furnaces is dealt with by J. E. Johnson, Jun.[1] The method of obtaining uniform distribution and a satisfactory working down of the charge are considered and various types of furnace tops are described and discussed. The same author has contributed a large number of articles on blast furnace practice which will be found in the numbers of Metallurgical and Chemical Engineering for 1915, 1916, and 1917. The methods used for charging blast furnaces in early English installations are described by F. C. Roberts[2] and these are compared with modern charging appliances as used in the United States. A mechanism has been patented by A. C. Nelson[3] for ensuring a better distribution of ore, coke, and limestone in blast furnaces, in which this distribution is accomplished by means of blades.

B. G. Klugh[4] deals with mechanical developments in the methods of sintering materials preparatory to blast furnace smelting. Types of appliances are described in which the storage bins are on the ground level and elevated above the ground level respectively.

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[1] *Met. and Chem. Eng.*, 1915, **13**, 161, 227.

[2] *Iron Age*, 1915, **45**, 192

[3] *Iron Trade Review*, 1917, **60**, 154.

[4] *Iron Age*, 1915, **96**, 1000 (Paper read before *Am. Iron and Steel Inst.*)

The use of rotary kilns for the agglomeration or nodulising of iron ores is described by S. E. Doak,[5] who states that desulphurisation can be combined with agglomeration, provided the kiln is sufficiently large and the sulphur does not exceed 6 to 7 . A kiln 60 feet by 5 feet is capable of treating 1500 tons of low-sulphur ore per month, and about half this quantity of high-sulphur ore.

The question of air supply for blast furnaces has received much attention and many descriptions of modern blowing plants have been given; among these may be mentioned the blowing and power plant installed by the Millom & Askam Hematite Iron Company.[6] There are three turbo-blowing sets, each capable of delivering 30,000 cubic feet per minute at 8 lb. pressure when running at 2800 revolutions per minute, at which speed the turbines develop 1280 brake-horse-power with a steam consumption of 13.9 lb. per brake-horse-power.

A description is also given of the blowing plant at the Barrow-in-Furness Works of the Barrow Hematite Steel Company.[7] This is the first plant arranged for supplying air to blast furnaces and Bessemer converters. When used for the blast furnaces air at 12 lb. pressure is supplied and for the Bessemer converters the air is delivered at 30 lb. pressure.

The theoretical considerations on which dry-air blast practice depends are discussed by J. E. Johnson, Jun.,[8] who describes a dry-air plant designed by F. C. Roberts & Co., and also the Carrier dry-air blast plant. The design of a recent two-stage compression refrigerating plant[9] by L. Sterne & Co. is also described and illustrated. The two-stage refrigeration adopted permits a reduction in the size of the plant, and the new Heenan cooler which is used, takes up less space than that required by the older pipe system.

B. F. Burnan[10] deals with the influence of composition of air-blast on blast-furnace working and points out that the amount of water-vapour present is most harmful. The water can be eliminated by cooling, but this is an expensive operation, and an alternative method is suggested which consists of employing a blast with graduated amounts of oxygen present. Formulæ for working out the necessary amounts of oxygen are given. The employment of oxygen blast for the blast-furnace and its effect on the furnace itself is also discussed by J. E. Johnson, Jun.[11] The effect of the enrichment of the blast by addition of sufficient oxygen to bring up the contents to 23% by volume is calculated by H. Blome.[12] The increase of oxygen increases the heat in the melting zone and reduces it in the shaft of the furnace, and can only be used with advantage on furnaces working with waste gas at a high temperature, and with charges so arranged to allow an increase in the indirect reduction of the ore. In these cases advantages will be obtained from a lowering of the waste gas temperature, a reduction in the carbon required for direct reduction, a reduced consumption of gas for heating the stoves, and reduced power for blowing.

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[5] *Trans. Am. Inst. Min. Eng.*, 1916, **53**, 144; *J.*, 1915, 1211.

[6] *Iron and Coal Trades Review*, 1917, **94**, 1.

[7] *Ibid.*, 1917, **94**, 96.

[8] *Met. and Chem. Eng.*, 1915,

[9] *Engineering*, 1916, **101**, 125, 152.

[10] *Met. and Chem. Eng.*, 1915, **13**, 624.

The present tendency is to increase the temperature of the blast in many iron furnaces, and in the manufacture of spiegel and ferro-manganese the maintenance of high blast temperatures is of particular importance. There is frequently, however, a very marked drop in the temperature of the hot blast between the stoves and the furnace. This is affected by the size and length of the hot blast mains and connections, thickness of the linings, volume and temperature of air passing, outside temperature, etc. R. J. Wysor[13] points out that insufficient insulation is the cause of this loss of heat and makes suggestions as to better methods of insulation.

The heat balance of a blast furnace stove has been worked out by R. S. G. Knight;[14] the final figures showing on the credit side, sensible heat in the gas 7·3%, heat of combustion of the gas 92·7%, and on the debit side, heat taken by blast 63·3%, heat taken by moisture in blast 2·6%, heat carried off by the products of combustion 29·1%, and heat lost by radiation 5·0%.

The cleaning of blast furnace gas has received a large amount of attention, and C. C. Lynde[15] shows that by washing the whole of the gas from blast furnaces, economies are secured in cost of operation, upkeep, relining of stoves, coke consumption, repairs to boilers, etc. The Brassert-Bacon washing and drying plant is described, and details are given of the mode of operation. At the South Works of the Illinois Steel Company,[16] the whole of the gas produced by the blast furnaces

[11] *Mech. Engineer*, 1915, **36**, 188 See *J*, 1915, 907

[12] *Stahl und Eisen*, 1915, **35**, 1028; *J, Iron and Steel Inst*, 1916, **93**, 331.

[13] *Trans. Amer Inst Min Eng.*, 1916, **53**, 373.

[14] *Carnegie Schol. Mem, Iron and Steel Inst*, 1916; **7**, 83.

[15] *Blast Furnace and Steel Plant*, 1916, **50**, 462.

[16] *Iron Age*, 1916, **97**, 53.

is washed. The Brassert two-stage system is used, in which vertical towers are employed, each tower being capable of dealing with the entire gas output of one furnace. Since the whole of the gas has been washed it has been found possible to maintain a temperature of 1200° F. from stoves which gave a temperature of 800° F. only with unwashed gas. The relative advantages of the dry hot and the cold wet methods of cleaning blast[17] furnace gas are discussed by L. Bradley, H. D. Egbert, and W. W. Strong, and the dry hot methods are shown to have many advantages over the wet methods. The electrical precipitation of dust in blast furnace gases by the Cottrell system has been used at the works of the Bethlehem Steel Company, and this was described by its inventor[18] at the annual meeting of the American Institute of Electrical Engineers. The principle on which the success of this process depends is that if a needle point be placed opposite a flat metallic plate, and the two be connected with the poles of a high-voltage direct-current supply line, the gas molecules between the point and the plate are charged with electricity and any dust particles are similarly charged, move towards the plate and stick to it

The possibility of recovering potash from blast furnace gases is of considerable importance in view of the present shortage, and C. Catlett[19] gives some approximate estimations of the amounts which could be saved, chiefly as potassium cyanide. The results of investigations on the recovery of potash from blast furnaces published by R. J. Wysor[20] are discussed by C. Catlett.[21] The investigations were carried out chiefly at the furnaces of the Bethlehem Steel Company where, during an examination of the efficiencies of the stoves, an analysis was made of the fine yellowish fume obtained from them. This fume was found to contain 15 of water-soluble potash. Pre-war prices did not justify the recovery of the potash, but since the commencement of the war, the dust has been disposed of at a good profit. The potash charged into the furnace as constituents of ores, fuels, and fluxes finds its way out, in chemical combination in the slag, as cyanide or other volatile or inflammable compound through the iron and cinder notches, by liquid exudation or decomposition from gas round the tuyeres, coolers, etc., by combination with the brickwork, as an accretion in the form of cyanide, and by evolution in the gas.

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[17] *Bull. Amer. Inst. of Min. Eng.*, 1917, **122**, 209

[18] *Iron Age*, 1915, **95**, 149 See also *J.*, 1916, 110

[19] *Iron and Coal Trades Review*, 1916, **93**, 154, from *Manufacturers' Record* Baltimore

[20] *Bull. Amer. Inst. Min. Eng.*, 1917, **121**, 1

[21] *Ibid.*, 83.

In the gas-cleaning practice at South Bethlehem there is a loss in the primary washers of over half the total potash charged, or about 12 lb. per ton of pig iron produced, and it appears that about two-thirds of the potash charged is now lost in the wash waters and stack gases.

The treatment of flue dust to render it suitable for subsequent blast furnace treatment has received some attention. The Baggaley[22] process consists in mixing it direct with molten iron. About 500 lb. can be treated per ton of iron used, and the product is said to be suitable for remelting at a minimum cost. The sintering plant of the Indiana Steel Co., for the treatment of flue dust is described by H. C. Estep.[23] This plant consists of two rotary kilns 90 feet long, and 9 feet in diameter. The flue dust enters at one end and slowly moves to the discharge end, the kilns rotating once per minute. Coke-oven gas is used as a fuel, the gas burner being introduced at the lower end. A scraper chain is provided in order to assist the passage of the material through the kiln and prevent it sticking to the sides. A briquetting press[24] suitable for dealing with flue-dust is also described. The economic handling of blast furnace slag is an important item, and the Croxton chain system of handling blast-furnace slag is described and illustrated by F. L. Prentiss.[25] The slag is run into beds across the bottom of which heavy chains are laid in parallel lines about 30 inches apart, with the ends extending upwards and out of the bed. After a time the ends of the chains are attached to a crane and pulled out through the slag, thereby breaking it up into small sizes which can easily be removed. A large amount of slag can be handled by this system with the minimum amount of dust and the avoidance of the disadvantages of steam which arise from the granulation of slag by means of water.

In foundry practice much attention has been paid to the introduction of iron turnings and scrap into cupola charges, and also to the introduction of steel scrap for the manufacture of semi-steel. A machine has been designed by the Stonehouse Works Company[26] West Bromwich, for bundling strip cuttings, scrap, and swarf. A bundle is made and withdrawn in two minutes, 2 horse-power being required to drive the machine." The use of pressed cast iron turnings in the cupola charge has been dealt with by R. Fichtner[27] in a series of articles.

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[22] *Iron Trade Review*, 1915, **57**, 358

[23] *Ibid.*, 1915, **56**, 1021

[24] *Iron Age*, 1916, **97**, 372.

[25] *Ibid.*, 1915, **95**, 1396 See also *Iron Trade Review*, 1915, **56**, 1318.

[26] *Iron and Coal Trades Review*, 1916, **93**, 155.

[27] *Stahl und Eisen*, 1916, **36**, 77, 181, 311, 411, 507. *Iron and Coal Trades Review*, 1916, **93**, 415.

The results of experiments carried out indicate that well pressed briquettes of cast iron turnings can be economically remelted in cupolas. Excessive loss was not found to take place with charges of pig and scrap with 30 % briquettes, although the total loss of iron increased proportionately to the addition of briquettes and the proportionate loss of silicon increased with additions of briquettes; the loss of carbon did not materially decrease nor did the amount of sulphur absorbed. The same subject received attention from J. A. Murphy[28] in a paper read before the American Foundrymen's Association at Cleveland, September, 1916, in which the practice of introducing borings and steel clippings into the cupola inside lengths of iron pipe is described.

The manufacture of semi-steel by the introduction of steel scrap into cupola charges has been described by D. McLain[29] and Y. A. Dyer[30] who give details of the requirements to be met and the tests obtained from suitable charges. Results obtained on a practical scale by the addition of varying quantities of steel scrap to cupola charges are given by G. S. Evans,[31] who shows that the chief causes of failure in the production of semi-steel are lack of proper attention to the cupola, improper composition of mixture, and incorrect pouring temperature.

G. Halston[32] gives the results of an investigation of liquid contraction in cast iron, in which he shows that a cast iron of a given composition has a certain range of casting temperature to produce a solid, dense, and strong casting free from liquid contraction. The iron used in the experiments contained about 2 % silicon and 1·4 % of phosphorus. R. H. Smith[33] shows, in a paper on sulphur in malleable cast iron, that contrary to the opinion generally held, sulphur is not removed during the ordinary annealing process for the manufacture of malleable cast iron. When conditions are such that the casting is oxidised, sulphur tends to segregate into the unoxidised portions. The author also states that sulphur does not appear to have any markedly injurious effects on the product until about 0·15 % is present, but that higher percentages give unsatisfactory bending tests and low deflections. In the discussion W. H. Hatfield pointed out that the average percentage of sulphur in Réaumur malleable cast iron is about 0·3 %.

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[28] *J. Iron and Steel Inst.*, 1917, **95**, 319.

[29] *Trans. Amer. Foundrymen's Assoc.*, 1917, **25**, 584.

[30] *Iron Age*, 1916, **97**, 542.

[31] *Ibid.*, 1916, **97**, 1541.

[32] *Carnegie Schol. Mem., Iron and Steel Inst.*, 1916, 7, 55.

[33] *J. Iron and Steel Inst.*, 1915, **92**, 141; *J.*, 1915, 1012.

PRODUCTION OF STEEL.

The development of the metal mixer since 1873 is dealt with by F. C. Thompson.[34] The usual capacity in this country is 150 to 300 ons, although the Ebbw Vale Works has one of 750 tons. Producer gas is mostly used in this country for heating the mixers whereas in America natural gas and oil fuel are most commonly used. Mixers are ound to give a surprising uniformity of product, the silicon and sulphur being reduced. The reduction of sulphur is due to the formation of manganese sulphide, which rises to the top and passes into the slag. The loss of iron in the mixer is estimated at 0·5% in unfired mixers and is probably very little higher in gas-fired mixers. A report dealing pecially with the design and sizes of metal mixers is given by F. Springorum[35] in which the cost of upkeep and working is dealt with. Comparative costs of firing with blast-furnace gas, producer gas, and oil uel are given.

Data showing the production of acid and basic Bessemer steel in he United States and in Great Britain are given by H. H. Campbell[36] which indicate that the acid process is being gradually displaced by the basic process. The method of shortening the blow in the Bessemer converter by the use of roll scale is discussed by A. Patton and F. N. Speller,[37] who conclude that better steel, increased production, and ower costs are obtained by its use. The best way of charging the scale s found to be into the empty vessel, before the charge of iron is poured n ; the iron used should be somewhat higher in silicon than for ordinary practice The addition of roll scale has been in use at the Ohio Works, Youngstown, for the last twenty years, where the increased production has amounted to about 25%. The nature and amount of the gases ssuing from converters are shown by G. Butz[38] to depend on the mpurities present in the iron, the weight of air required in the process, and the temperature of the gases. The author calculates the heat-energy evolved during the process and shows that if only 10% of this heat could be utilised it would reduce the cost of ingots by nearly s. 6d. per ton.

The method of manufacturing pure iron in the open-hearth furnace s described by H See.[39] The charge consists of 15,000 to 18,000 lb.

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[34] *Iron and Coal Trades Review*, 1915, **91**, 33.

[35] *Stahl und Eisen*, 1915, **35**, 825, 825; *J. Iron and Steel Inst*, 1915, 92, 262.

[36] *Iron Age*, 1916, **98**, 302.

[37] *Bull. Amer. Inst. Min. Eng*, 1917, No. 122, 139.

[38] *Iron Age*, 1915, **95**, 618.

[39] *J. Assoc. Eng Societies; J. Iron and Steel Inst*, 1915, **92**, 277.

of limestone and 150,000 lb. of mixed pig iron and scrap. Oxidation of impurities is partly effected by additions of iron ore, but the furnace used is also equipped with air blast to assist this oxidation. Seven to eight hours is occupied in the melting down of the charge, the air blast is then turned on and iron ore added from time to time until the impurities are reduced to mere traces. The average time occupied per heat is twelve hours, and aluminium is used as a deoxidizer. A typical analysis is given as follows: C 0·01, Si 0·001, S 0·025, P 0·005, Mn 0·025%.

Various improvements in the design of details of open-hearth furnaces have been described, including the Schumann[40] device for reversing the direction of the gases. This device is controlled by a clock, the hour hand of which forms a contact operating a solenoid and raising a plunger which opens a four-way valve and controls the passage of air and water in a pipe system. The Blair[41] method of reversing by means of brick-lined tubes is also described.

An illustrated description of the Wiegand[42] chain screen doors for furnace openings is given. These consist of strands of steel chain freely hanging from a bar in such a manner as to form a continuous curtain. This curtain, hung before the open door of the furnace, hinders heat and gases from leaving the furnace and cold air from entering, and at the same time protects the workmen from the glare without offering any serious obstruction to the introduction of tools, etc. The Orth[43] system of reinforced concrete for open-hearth furnace roofs is described, and it is stated that by the introduction of this method the number of heats per roof has been increased from 387 to 537.

The essential features of checker brick arrangements in regenerators are discussed by W. A. Janssen,[44] who shows that they should offer a maximum area for heat absorption and a minimum retardation to the flow of gas. The facility with which cleaning operations can be carried out is very important. The design of regenerators is dealt with, and it is shown that length, breadth, and depth are important factors. Silica bricks, although more expensive, are more efficient than ordinary firebricks. The question of the deterioration of refractory materials with special reference to open hearth practice is the subject of an investigation by H. B. Cronshaw.[45] The principal causes of destruction in the various parts of open hearth furnaces are enumerated and the effects they produce are discussed. In the roof of the furnace, which is the most vulnerable part, all the erosion which occurs can be attributed to the effects of abrasion, volume changes, and the action of heat and fluxes. The principal source of trouble is the dust which is derived partly from the producers and partly from the charges. The deterioration of the port blocks and regenerators also receives attention. In the latter, the dust is particularly troublesome and this is specially the case in basic furnaces where the dust consists mostly of ferric oxide and lime, derived from the charges. In a second paper[46] on this subject, the same author deals further with the deterioration of the regenerators and roofs of open-hearth furnaces and also discusses the refractories used in blast furnaces and cupolas. The standardisation of refractories is discussed under the following heads: Mineral composition, permeability, resistance to temperature changes, dilatation, permanent expansion and contraction, hardness, toughness, and crushing strength.

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[40] *Met. and Chem. Eng.*, 1916, **14**, 111

[41] *Iron Trades Review*, 1916, **58**, 138

[42] *Met. and Chem. Eng.*, 1915, **13**, 875

[43] *Iron Age*, 1915, **96**, 1284

[44] *American Foundrymen's Association*, Sept. 1915. *J. Iron and Steel Inst.*, 1915, 92, 278.

The results of experimental work on different forms of burners used for powdered coal as a fuel for open-hearth furnaces are given by C. J. Gadd,[47] who sums up the chief points as follows: (1) The fuel is burnt above the bath and all the heat contained in the coal is instantly developed in the furnace; (2) as the path of the flame is in one direction, all parts of the furnace are maintained at the same temperature; (3) on account of their high radiating capacity, the infinite number of minute incandescent particles in the powdered coal communicate the heat by radiation and not by convection, and it is not necessary therefore to bring the surrounding air to the temperature of the coal particles; (4) all the heat in the waste gases is conserved and can be used in the production of steam.

The development and use of modern waste heat boilers in connection with open hearth steel furnaces, etc., are dealt with by A. D. Pratt[48] In modern waste heat boilers an induced draught is used to produce the gas velocity necessary for a satisfactory rate of heat transfer; in some cases this improves the operation of the open-hearth furnace. In the case of open-hearth steel furnaces the power obtained by using the waste heat is equivalent to a reduction of from 10d. to 1s. per ton of steel produced. The first installation of boilers for utilising the waste heat from open-hearth furnaces in the United States was put in operation in 1910 at the South Chicago Works of the Illinois Steel Co. The results of a month's test showed an output of 190 boiler horse-power during the furnace heat with gas at a temperature of 1150° C., and encouraged the installation of other boilers. C. J. Bacon[49] deals with the case of an installation of twenty-eight boilers, in which the heat recovered is about 22% of the heat in the coal charged into the producers, or from 1,600,000 to 2,200,000 B.Th.U. per ton of ingots.

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[45] *Carnegie Schol. Mem., Iron and Steel Inst.*, 1916, **7**, 18.

[46] *Ibid.*, 172.

[47] *J. Franklin Inst.*, 1916, **182**, 323; *J.*, 1916, 1065

[48] *Amer. Soc. Mech. Eng.*; *Met. and Chem. Eng.*, 1916, **15**, 696. *Ibid.*, 1917 **16**, 27.

A detailed account of the duplex process as carried out at the works of the Lackawanna Steel Company is given by G. B. Waterhouse.[50] The plant comprises 12 cupolas, 4 12-ton converters, 2 mixers, 250 and 300 tons respectively, 2 large tilting furnaces, and 8 stationary 100-ton furnaces. F. F. Lines[51] deals with the duplex process in a paper read before the International Engineering Congress at San Francisco, and states that the process shortens the duration of the purification in the open-hearth by about five-sixths. H. H. Campbell[52] shows that the Duplex process produces more scrap than it consumes, and that this independence of scrap supply has made it possible to produce steel as cheaply as in the converter in large well-equipped plants. The details of the Duplex process are also discussed by various authors, and S. S. Martin[53] deals with the conditions necessary for the successful working of the process. He points out that subsidiary operations in the Bessemer plant should provide an ample supply of metal, and advocates three 20-ton converters where 50-ton open-hearth furnaces are employed. It is necessary that the metal should contain sufficient heat-producing elements to prevent skulling in the duplex ladle, while for rapid working in the open-heath the metal must be charged at a temperature near the correct open-hearth tapping temperature. The function of manganese in the duplex process is shown by J. I. Peyton[54] to be of greater importance than in the "straight" open-hearth process. The same author points out that in order to carry out the process economically, large units situated close together are necessary in order to reduce waste and labour costs.

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[49] *Amer. Iron and Steel Inst.*, *Iron Age*, 1915, **95**, 1349; *J. Iron and Steel Inst.*, 1915, **92**, 279.

[50] *Iron Age*, 1916, **98**, 999, 1035.

[51] *Met. and Chem. Eng.*, 1915, **13**, 656.

[52] *Iron Age*, 1916, **98**, 149.

[53] *Ibid.*, 1915, **95**, 75.

[54] *Met. and Chem. Eng.*, 1915, **13**, 397.

The relative merits of the various agents used for the deoxidation of steel have been studied by H. M. Boylston.[55] The effect of the following deoxidisers received attention: ferro-manganese, ferro-silicon, ferro-carbon-titanium, carbon-free ferro-titanium, and aluminium. The first series of tests was carried out with raw converter-metal and the second series with 0·5% carbon steel. As a result of these experiments, no startling differences were observed by using the different deoxidising agents; the results, however, are not conclusive, although judging by the soundness of ingots produced, the following is the order of merit obtained: aluminium, ferro-silicon, ferro-titanium, ferro-carbon-titanium, ferro-manganese.

A. W. and H. Brearley[56] deal with some properties of ingots in which they consider crystalline structure and its effects on the solidification of ingots, shrinkage and contraction cavities, casting temperature, etc. Some interesting results are recorded from experiments on the solidification of wax which are used to illustrate the mode of solidification of steel ingots. Two papers dealing with steel ingot defects are published by J. N. Kilby,[57] in the first of which bottom casting, top casting, and tun dishing for top poured ingots are dealt with. In the second paper it is shown that a good percentage of the defects in steel ingots come under the following heads:—Pipe, segregation, occluded slag, fluxed fireclay, lappiness, cracks. These defects are dealt with in detail and tables are given showing the relation between speed of teeming and number of cracked ingots produced.

PHYSICAL PROPERTIES, HEAT TREATMENT, ETC., OF IRON AND STEEL.

An interesting paper on the use of meteoric iron by primitive man by G. F. Zimmer[58] includes a table containing all the well known meteoric irons, siderites, and siderolites.

F. C. Thompson[59] contributes a very important theoretical paper on surface tension effects in the intercrystalline cement in metals and the elastic limit, in which he adopts and utilises the theory that surface-tension forces act within the amorphous modification between the grains of a metal. By this means an explanation of elastic limit, yield point, and the chief effects of strain is obtained. In a further paper by the same author[60] on the influence of surface tension upon the properties of metals, especially of iron and steel, various questions which arose during the discussion of the previous paper are dealt with and some effects of surface tension on steel are described.

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[55] *Carnegie Schol. Mem., Iron and Steel Inst.*, 1916-7, 102, 133

[56] *J. Iron and Steel Inst.*, 1916, **94**, 137; *J.*, 1916, 1018.

[57] *Ibid*, 1916, **94**, 193; 1917, **95**, 69; *J.*, 1917, 530.

[58] *Ibid*, 1916, **94**, 306.

[59] *Ibid.*, 1916, **93**, 155.

[60] *Ibid.*, 1917, **95**, 155.

J. E. Stead contributed a paper on the influence of some elements on the mechanical properties of steel, which gave rise to a considerable amount of discussion. The elements considered were carbon, phosphorus, sulphur, manganese, silicon, copper, and tin.[61] A bibliography of literature on the relations of chemical composition and physical properties of iron and steel is appended to the paper.

W. Austin[62] gives the results of some experiments on the influence of oxygen on some properties of pure iron for which the specimens were prepared by melting iron and iron oxide in a small Girod furnace. No difference could be detected between the melting points of pure iron and the specimens containing 0·28 % oxygen. The material can be forged and rolled, the latter operation being carried out above 950° or between 750° and 850° C. Difficulty in working the material was experienced in the neighbourhood of 900°. Contrary to expectation, the oxygenated metal resisted atmospheric corrosion quite well. The oxygen content of iron and steel and its effect on their properties have been studied by J. Allen Pickard,[63] who has previously reported on the oxygen content of the open-hearth steels. The steels now examined and the oxygen contents found are as follows: Acid Bessemer, 0·006 to 0·018; basic Bessemer, 0·010 to 0·077, crucible steel, 0·001 to 0·017; wrought iron, 0·136 to 0·203; ingot iron, 0·020 to 0·092; cast iron, 0·017 to 0·021. About 0·405 % of ferrous oxide is soluble in liquid steel nearly free from other impurities. Oxygen when present to an extent exceeding 0·01 % tends to produce brittleness under shock.

The nature of the scale which is formed on a 3 to 4 % nickel steel on heating to between 800 and 1100° C. is described by J. E. Stead,[64] who shows that the concentration of nickel in the outer layers of nickel steel when long heated at about 800–1000° C. is due to interdiffusion of iron and nickel and the removal of iron as oxide at the surface of the metal. The oxidation follows the crystal junctions of the metal and the grains become surrounded by oxide. As a result of the above observations, experiments were carried out on the reduction of oxides of nickel and copper by means of iron, which showed that solid iron is capable of reducing oxides of nickel and of copper with the formation of iron oxide. This interchange is not confined to the surfaces of contact, but extends for a considerable distance from the surface of the iron, suggesting that there is interdiffusion of iron and nickel and iron and copper and of the oxides of these metals.

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[61] *J. Iron and Steel Inst.*, 1916, **94**, 5; *J.*, 1916, [illegible]86.

[62] *Ibid.*, 1915, **92**, 157; *J.*, 1915, 1011.

[63] *Carnegie Schol. Mem., Iron and Steel Inst.*, 1916, **7**, 68.

[64] *J. Iron and Steel Inst.*, 1916, **94**, 243; *J.*, 1916, 1018.

The question of the occurrence and influence of nitrogen on iron and steel is the subject of a paper by N. Tschischewski[65] (Tomsk) in which our knowledge of the subject is increased; at the same time the evidence put forward is still insufficient to decide definitely whether the small quantities of nitrogen met with in commercial iron and steel have serious injurious influences on the mechanical properties. The author suggests that nitrogen is introduced into steel by the addition of ferro-manganese, ferro-silicon, and aluminium when these are used as deoxidants and proves the existence of manganese, silicon, and aluminium nitrides as definite compounds. During the discussion of the paper J. E. Stead indicated that the results of an elaborate research on the effect of nitrogen on steel may be published shortly, as work on this subject is being carried out by a small self-elected committee of members of the Institute.

The gases occluded in alloy steels have been examined by J. W. Donaldson[66] who finds that the volume of the gas dissolved in alloy steels diminishes, according as to whether the special element is nickel, silicon, chromium, or manganese. The nature of the dissolved gases is similar to those of ordinary steel, except that silicon and manganese decrease the amount of carbon dioxide present while increasing the amount of hydrogen. Chromium tends slightly to increase the amount of nitrogen. The largest quantities of gas are evolved in the neighbourhood of the critical points or over the critical ranges, the special steels behaving like ordinary carbon steels in this respect.

The effect of slag inclusions on the structure of nickel steel has been studied by F. Giolitti and Zublena[67] The steel contained about 2% of nickel and the light grey inclusions were found between the ferrite borders and separate from the pearlite. After heating to 1060° for four hours the inclusions were no longer separated from the pearlite and after heating to 1100° and 1190° the inclusions were not surrounded by ferrite. It is thus possible that the injurious effects of slag inclusions can be eliminated by suitable heat treatment.

Certain inclusions in steel have been studied by A. McCance,[68] who shows that very often the light coloured inclusions which are considered to be manganese sulphide consist of manganese and aluminium silicates containing manganese sulphide in solution. A sample of the scum which sometimes floats on the surface of molten steel was found to be similar in composition, but with the ferrous oxide partly replacing the manganese sulphide. Many non-metallic particles found in steel are of the order of 0.001 inch in diameter and their rate of rising in the steel is so slow that they are largely trapped in the solid metal.

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[65] *Ibid.*, 1915, **92**, 47; *J.*, 1915, 1012.

[66] *Carnegie Schol. Mem., Iron and Steel Inst.*, 1916, **7**, 41.

[67] *Int. Zeits. Metallog.*, 1914, **7**, 35; *J.*, 1916, 257.

[68] *J. West of Scotland Iron and Steel Inst.*, 1916-17, **24**, 55.

G. F. Comstock[69] also points out that all the light grey inclusions in steel are not necessarily manganese sulphide, as iron oxide may assume a similar appearance. The best method of distinguishing the two is by means of a boiling solution of alkaline sodium picrate which darkens sulphide inclusions but leaves the oxides unattacked. The same author[70] deals with the presence of alumina in steels. He shows that the differences between inclusions of alumina and of ordinary slag in steels are as follows:- Alumina is very hard to polish without pitting, whereas silicates take a good polish; silicates are also elongated in the direction of rolling or forging whereas alumina particles are not; silicate inclusions are frequently of large size while alumina particles are not, and they do not seem to coalesce into large bodies even when closely grouped together. A. Sauveur[71] follows this investigation by the examination of a number of samples of thermit iron melted with aluminium and with alumina, and confirms Comstock's work by showing that alumina inclusions can be detected under the microscope from the other inclusions by their small size, their dark coloration, and more especially by a complete absence of elongation in the direction of rolling or forging.

An interesting note on the carburisation of iron at temperatures of about 500° C. in blast furnaces gases has been communicated by T. H. Byrom,[72] who showed that when iron was exposed to the action of these gases carbide of iron was formed; in some cases the amount of carbon on the outside layers reached nearly 7%. Confirmatory experiments carried out by J. E. Stead are also described and an interesting discussion followed the reading of the paper. J. E. Stead[73] has since examined the effect of blast furnace gases on wrought iron at temperatures between 400° and 500° C., leaving the iron exposed to the action of the air for nearly two years. The results show that the iron itself is not carburised under these conditions, but iron scale and magnetic cinder react with carbon monoxide inducing carbon to be deposited on the surface.

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[69] *Bull. Amer. Inst. Min. Eng.*, 1916, 2103.

[70] *Met. and Chem. Eng.*, 1915, **13**, 891; *J.*, 1916, 59.

[71] *Met. and Chem. Eng.*, 1916, **15**, 149; *J.*, 1916, 929.

[72] *J. Iron and Steel Inst.*, 1915, **92**, 106; *J.*, 1915, 1012.

[73] *Ibid.*, 1916, **94**, 249; *J.*, 1916, 1018.

The results of experiments on cementation by gas under pressure are given by F. C. Langenberg.[74] The pressure furnace as used in the Harvard University is described, and the results obtained by the use of illuminating gas and acetylene show that no carburisation occurred below 720° C. and that at the γ-β range sharp breaks in the carburisation curves occur. The effect of pressure on the degree of carburisation was ascertained and was found to vary at different temperatures in the case of illuminating gas. There are also indications that after a certain pressure is reached, further increase of pressure will not cause additional absorption of carbon by the iron.

A new thermo-electric method of studying allotropic changes in iron and other metals is described by C. Benedicts.[75] In this method the metal to be investigated is moved in the form of a wire with constant speed through a small furnace, the maximum temperature of which is known; between the free ends of the wire an electro-motive force may appear if molecular changes occur in the metal at temperatures below the maximum.

A sensitive method for the thermo-electric measurement of the critical ranges of pure iron is described by G. K. Burgess and H. Scott,[76] and the results of the observations are given. An apparatus for the measurement of the electrical resistance at high temperatures and its application to the determination of the critical points of iron and steel is described by D. Saldau.[77] Results of the determination of the line of transformation and of the solubility of cementite are given, the latter showing a straight line. In the γ-range a new boundary line is indicated at 980° C.

An electro-magnet method for determining the critical point in the heat treatment of steel is described by R. B. Fehr,[78] the main features of which are the use of a source of magnetic flux located outside the furnace, a small test coil slipped over the outside end of a small diameter steel rod which is in contact with the steel undergoing treatment, and a dead-beat galvanometer in the test coil circuit for indicating the change of magnetic properties.

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[74] *Ibid.*, 1917, **95**, 129; *J.*, 1917, 530.

[75] *Ibid.*, 1916, **93**, 211; *J*, 1916, 362.

[76] *Ibid.*, 1916, **94**, 258; *J.*, 1916, 844.

[77] *Carnegie Schol. Mem*, *Iron and Steel Inst*, 1916, **7**, 195. See *J.*, 1916, 1116; 1917, 1010.

[78] *J. Iron and Steel Inst.*, 1917, **95**, 203.

The results of an investigation on the properties and microstructure of eutectoid carbon steel and the position and length of Ar. 1 and how these are affected by the conditions of heating and cooling, are published by H. M. Howe and A. G. Levy.[79] The same authors deal with the influence of quenching temperature and time of tempering on the properties of eutectoid carbon steel.[80]

The determination of the cementite line in the iron-carbon diagram has been carried out by N. Tschischewsky and N. Schulgin[81] by etching sections at high temperatures in *vacuo*. The arrangements necessary for the work are described, chlorine being used as the etching reagent. Detailed results are given which again indicate that the cementite line from 700 to 1130° C. is a straight line

K. Honda and H. Takagi[82] have determined the transformation temperature of cementite and show that on cooling, the magnetic transformation begins at 215° C. and on heating, it ends at the same temperature. The transformation takes place gradually, at least in a range from 50° to 60° C.

The influence of heat treatment on the thermo-electric properties and specific resistance of carbon steels is dealt with by E. D. Campbell,[83] who attributes the changes brought about by tempering and annealing hardened steel to the precipitation of the carbides

The transformations of special steels have been studied by K. Honda, K. Tawara, and H. Takagi,[84] the steels used containing varying quantities of chromium, tungsten, molybdenum, and vanadium.

J. H Andrew[85] has carried out investigations of iron-carbon-silicon alloys in which the procedure adopted was to take a series of freezing curves of different alloys under different conditions and to supplement the results obtained by the micro-examination of the variously treated specimens. The results indicate that carbide of iron is unstable below 700° on cooling, breaking up extremely slowly into α-iron and free carbon. The photomicrographs show that carbide of iron separates from the melt even in the case of the alloy containing 9 86% of silicon and that this carbide can exist undecomposed down to a temperature which is in all probability about 1100° C.

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[79] *Ibid*, 1916, **95**, 210, *J*, 1916, 1063

[80] *Proc Amer Soc for Testing Materials*, 1916, **16**, Part II, 7

[81] *J Iron and Steel Inst*, 1917, **95**, 189; *J*, 1917, 531

[82] *Ibid*, 1915, **92**, 181, *J*, 1915, 1011

[83] *Ibid*, 1916, **94**, 268; *J*, 1916, 1018

[84] *Ibid*, 1916, **93**, 224; *J*. 1916, 844

[85] *Carnegie Schol. Mem*, *Iron and Steel Inst*, 1916, **7**, 1

The heat treatment of large forgings is the subject of a paper by W. Beardmore[86] in which it is shown that the principles involved are the same as those which apply to small forgings. The object of such heat treatment is to confer on the forgings the least crystalline growth or the smallest grain size. At any given temperature the time the material is kept at that temperature, and the time taken in cooling it down, have a very important influence on the grain size. There is a limit in the size of the forgings beyond which a plain carbon steel cannot be used with safety and an alloy steel must be used. The effect of work is very important and there is an intimate connection between the grain size and the amount of work during forging. H. H. Ashdown[87] also deals with the heat treatment of large forgings and illustrates the types of structure obtained in steels subjected to various heat treatment by means of photomicrographs.

C. P. Sandberg[88] describes his process for the surface hardening of rails. The process depends on the fact that if the steel whilst still above the critical range is treated with air, steam, atomised water, or brine on the surface in such a manner as to cool it down moderately slowly, the desired hard and tough sorbitic structure is obtained. The process is applied after the rolling operation is completed or, in a modified form, on the surface of worn train-rails without removing them from the track.

A description of the Vickers surface-hardening process[89] shows that this process consists of the application of an intensely hot flame from an oxy-acetylene blowpipe momentarily to the surface of the part to be treated, the necessary quenching effect being produced by the absorption of the heat by the cold body of metal beneath the surface. The process is used largely for gear-tooth hardening.

In notes on quenching, L. H. Fry[90] describes experiments carried out with the object of studying the rate of cooling in various quenching media and ascertaining the relation between rate of cooling and the physical properties obtainable in quenched and tempered forgings. The influence of the form of the object on the rate of cooling is dealt with and the relation between the quenching speed and the composition of the medium. It is suggested that for rapidity of cooling it is necessary to have intimate contact between fluid and object in order to allow transfer of the heat from the object to the fluid, and a free flow to remove heated and vaporised fluid from the surface of the object.

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[86] *Proc. Inst Mech Eng*, 1917, Jan -May, 215; *J.*, 1917, 459.
[87] *Proc. Inst Mech Eng*, 1917, Jan.-May, 225; *J*, 1917, 458.
[88] *Foundry Trade J*, 1916, **18**, 548.
[89] *Iron and Coal Trades Review*, 1917, **94**, 5.
[90] *J Iron and Steel Inst*, **1917**, **95**, 119; *J*, 1917, 531

A great acceleration in cooling is produced by a forced agitation of the fluid.

C. A. Edwards and H. Kikkawa[91] have studied the effect of chromium and tungsten upon the hardening and tempering of high-speed tool steel, and have shown that the first effect of tempering hardened high-speed steels is to make them softer, but when they are tempered at higher temperatures they again become harder and after heating to 614° C. they are much harder than in the initial air-quenched state. Chromium in conjunction with carbon is the cause of the great hardness of hardened high-speed steels; it materially lowers the temperature at which these steels can be air-hardened. In the absence of chromium, tungsten raises the temperature at which tempering and annealing begin and in the presence of chromium it increases the intensity of the secondary hardening and raises the tempering temperature. Tungsten steel containing 18% of tungsten and 0·63% of carbon can be air-hardened only by rapid air-quenching from temperatures above 1050° C. The maximum resistance to tempering and the greatest degree of secondary hardening can only be obtained by getting the tungsten into solution, and with modern high-speed steels this is not complete until a temperature of about 1350° C. is reached.

In a further paper on the initial temperature and critical cooling velocities of a chromium steel, C. A. Edwards[92] with J. N. Greenwood and H. Kikkawa confirms the contention that chromium imparts the property of self-hardening to steel. He worked with a steel containing about 5% of chromium and shows that the property of self-hardening is governed by the rate of cooling. The critical cooling velocity however, varies with the initial temperature, being much slower as the temperature is raised.

The penetration of the hardening effect in chromium and copper steels has been studied by L. Grenet,[93] who concludes that copper increases the depth of hardening effect in steels and that the influence of copper in the presence of chromium is marked.

The influence of carbon and manganese upon the corrosion of iron and steel has been studied by R. Hadfield and J. Newton Friend,[94] who show that the addition of successive amounts of carbon to pure iron containing less than 0·2% of manganese results in a steadily increasing rate of corrosion to a maximum with 0·8% of carbon in dilute sulphuric acid. The addition of 0·7% of manganese to the carbon steels results in a very slightly increased corrosion in sea and tap water and an enormously increased corrosion in dilute sulphuric acid. By increasing the manganese to 2% and upwards the corrodibility in water is greatly decreased and in sulphuric acid is greatly enhanced.

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[91] *Ibid.*, 1915, **92**, 6; *J.*, 1915, 1013.

[92] *Ibid.*, 1916, **93**, 114; *J.*, 1916, 603.

[93] *Ibid.*, 1917, **95**, 107; *J.*, 1917, 530.

[94] *Ibid.*, 1916, **93**, 48; *J.*, 1916, 603.

The theory of the corrosion of steel is dealt with by L. Aitchison,[95] who concludes that the corrosion of steel takes place purely by the action of the ferrite or the solid solution. In order that a third element in a carbon steel shall have a beneficial effect, it is necessary that the proportion of this element should be sufficient to produce a fairly high percentage in the solid solution. He also concludes that the deciding factor in the corrosion of a steel is the electromotive force of the solid solution with respect to the corrosive liquid, that the pearlite of a steel does not corrode as a whole, and that carbides are not decomposed by ordinary corrosive agents, but that they merely act as cathodes to the anodes of ferrite or solid solution.

The preservation of iron and steel by means of passivifying factors has been studied by T. G. Thompson,[96] who shows that at atmospheric conditions the introduction of varying amounts of potassium bichromate into solutions of different concentrations of sodium sulphate, sodium chloride, magnesium sulphate, magnesium chloride, and calcium sulphate, inhibits corrosion to a remarkable extent. Differences in chemical composition and physical properties of the iron and steel employed seemed to have practically no effect. In spite of these facts the commercial application of potassium bichromate to boiler waters is not considered practicable because of cost and uncertainty of results. The action of disodium phosphate was also examined.

The corrosion of cast iron has been studied by O. Bauer and E. Wetzel.[97] Cast iron when embedded in moist soil is subject to a form of corrosion known as graphitisation, iron cancer, etc., by which it is converted locally into a soft friable grey mass. A fundamental condition for corrosion of this type is the presence of liquid water. The corrosion is accelerated by electric currents The oxidation products of the iron are retained in position by the network of graphite in the case of grey irons and by the network of cementite in the case of white irons.

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[95] *Ibid*, 1916, **93**, 77; *J*, 1916, 603.

[96] *Carnegie Schol. Mem*, *Iron and Steel Inst*, 1916, **7**, 232

[97] *Mitt K. Materialpruf*, 1916, **34**, 11; *J*, 1916, 1112

The presence of copper in steel appears to reduce its liability to corrosion as shown by E. A. and L. T. Richardson[98] during a discussion of the subject of corrosion before the American Electro Chemical Society, and the results of further recent tests[99] also confirm this statement.

The various methods used in the welding of metals has received a considerable amount of attention In the pencil electrode method of welding, as described by E A Wildt,[100] only just sufficient heat is obtained to accomplish the joining of the two metals. A high temperature is prevented because, as fast as the metal wire used as part of the circuit becomes plastic, the pencil must be advanced to close up the spark gap. A report on the arc-welding process has been published by the Association of Railway Electric Engineers[101] in which it is shown that the amount of heat which can be applied depends on the size of the electrode, the nature of the welding wire and the nature of the piece to be welded. It is shown that three important changes occur in the metal during the welding operation The effects of mechanical treatment are eliminated, the metal is oxidised and rendered cold short unless it is protected by a covering of slag, and a varying proportion of the impurities present in the steel is oxidised and removed.

A comparison of the costs of oxy-hydrogen and oxy-acetylene cutting is made by W P. Schuck,[102] and H. R Swartley, Jun.,[103] deals with recent progress in the use of oxy-hydrogen and oxy-acetylene for welding and cutting of metals.

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[98] *J*, 1916, 1158

[99] *Foundry Trade J*, 1916, **18**, 429

[100] *J Amer. Soc. Mech Eng*, 1917, **39**, 46

[101] *Power*, 1916, **44**, 766.

[102] *Met. and Chem. Eng*, 1916, **15**, 218

[103] *Iron Age*, 1915, **96**, 1122, from International Engineering Congress

METALLURGY OF THE NON FERROUS METALS.

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THIS review deals with the general metallurgy of the non-ferrous metals other than those which have an important application in the manufacture of alloy steel. It is not claimed that it is exhaustive, for apart from the limited space available there is the fact that certain developments must, owing to present exigencies, be considered as secret.

GOLD.

There have been no notable developments in the metallurgy of gold during the period under review, but considerable development has been made in the improvement of recognized standard methods.

The cyanide process, with the various modifications connected therewith, still holds the premier place in the methods of extracting gold from its ores.

Amalgamation is still employed, especially where the metal is coarse; and F. A. Thomson and R. Keffer[1] have shown that in the presence of sulphates of iron, manganese, and zinc, amalgams are superior to pure mercury for this purpose. It is considered that this superiority is due to their greater resistance to coating, cadmium amalgam being the most resistant, followed in order by lead, tin, gold, silver, sodium, zinc. F. B. Sanford[2] claims that the treatment of concentrates with an aqueous solution of ammonium chloride and sodium phosphate at about 115° F., renders them amenable to amalgamation.

The Geliens[3] process for the treatment of refractory gold-silver-copper ores consists of sliming the ore, after the removal of soluble sulphates, and then amalgamating in a special amalgamator in the presence of caustic soda. At a later stage potassium chlorate is added and the pulp aerated. Aeration causes the oxidation of the sulphides and the consequent formation of sodium bisulphate, which reacts with the chlorate on the complex gold and silver compounds, leaving the precious metals in an amalgamable condition. The free gold is amenable to amalgamation after the addition of the alkali, the complex compounds of silver after chlorate has been added, and the silver sulphide after the formation of the bisulphate. The process is suitable for ores containing pyrites, blende, mispickel, sulpho-tellurides, etc.

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[1] *Met. and Chem. Eng.*, 1915, **13**, 367; *J.*, 1915, 719

[2] U.S. Pat. 1176858, 1916, *J.*, 1916, 606.

[3] *Min. and Eng. World*, 1915, **43**, 473; *J.*, 1915, 1095

In connection with the cyanide process various causes are given, including hydrolysis, for cyanide losses.[4] It still seems questionable whether the loss supposed to be due to hydrolysis is not the result of the action of carbon dioxide.

The principle of the counter-current decantation process, or the C.C.D. process as it is now termed, has been known since 1901. There is a possibility of this method replacing leaf filters as judged by the results of the plant in operation at the Hollinger Co's. works.[5] The cost worked out to be about 10 of the cost of filtering with leaf filters as taken over a period of 12 weeks.

Precipitation by means of zinc still remains the most largely used method for the recovery of gold from cyanide solutions. Additional tests[6] have been carried out by N. Herz on the use of zinc dust, and these may lead to the further utilization of this material, although according to Irvin[7] zinc thread is generally used, as it is a question of capital outlay.

H. R. Conklin[8] describes a method of precipitating gold and silver from cyanide solutions by means of moving zinc balls in an inclined zinc-lined cylinder; this may prove to be a valuable innovation Electrolytic precipitation is stated by G. H. Clevenger[9] to be less complete than precipitation by zinc, and for the sake of economy it is better to precipitate partially by electrolysis and complete the precipitation in zinc boxes. On account of the low conductivity the electrodes are placed only 1½ inches apart. Lead is the usual material used for cathodes, and in American practice it is also used for anodes, whereas on the Rand iron anodes are employed.

The conversion of precipitate to bullion is an extensive problem on account of the varying composition of the material obtained from the clean-up. It has been found[10] that the residual slime from the usual acid treatment, if agitated with sulphuric acid and potassium bichromate, yields a bullion practically free from zinc, lead, and copper after fusion with nitre and borax J. Penhale[11] has patented a process for treating zinc-gold slime which consists of mixing the dry material with about 10% its weight of litharge and an excess of carbonaceous material and retorting this mixture, whereby zinc is distilled off and lead bullion left behind.

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[4] H A White, *J Chem Met and Min Soc, S. Africa*, 1915, **16**, 24, *J*, 1915, 1254 [5] L B Eames, *Met and Chem Eng*, 1917, **16**, 94, *J*, 1917, 220

[6] *Min and Eng World*, 1915, **43**, 769; *J*, 1915, 1254

[7] *Min. and Sci Press*, 1916, **112**, 115.

[8] *Eng. and Min J*, 1917, **103**, 195; *J*, 1917, 292.

[9] *Eng. and Min J.*, 1916, **102**, 579; *J*, 1916, 1114.

[10] *Eng. and Min J*, 1915, **100**, 523; *J.*, 1915, 1056.

The treatment of by-products from the Tavener process has been confined in the past very largely to the blast-furnace, but at the Alaska Treadwell mine this has been superseded by an electric furnace.[12] The furnace is operated on the lighting circuit through a 50-kilowatt transformer. The charge consists of old reverberatory hearths, litharge, coke, scrap iron, and refinery by-products. The advantages claimed over blast-furnace practice are a considerable reduction in the mechanical loss of gold in flue dust, a clearer slag free from metal shots, almost complete control over the melting temperature, and improved working conditions for the operators.

According to J. H. Hance,[13] bullion bars obtained from "cyanide" gold show variations in composition due to segregation, and this is well marked when the metal is practically free from silver. If, however, 9% to 10% of silver is present the bars are homogeneous.

Turning now to the treatment of complex ores, K. B. Moore and H. R. Edmands[14] state that certain arsenical-antimonial-sulphide ores only yield 50% of their gold content when treated by ordinary methods such as amalgamation, cyanidation, etc., but after fine grinding, roasting sufficiently to liberate the gold from the sulphides, mixing with oxidised ores, and agitating with sodium sulphide, cyanide extractions of over 80% can be obtained. The cyanide consumption is equal to about 1 lb., and the cost 9*s.* per ton of ore.

In a report on the treatment of antimonial gold ores from the Murchison range, H. R. Adam[15] shows that where antimony is not much above 1%, gold can be extracted with fair success by the usual methods, but, as might be expected, the cyanide consumption is always high.

Flotation tests made by F. Wartenweiler,[16] using a mixture of wood creosote and paraffin on arsenical pyritic ore from Barberton, Transvaal,

[11] Eng. Pat 14921, Oct. 21, 1915, *J.*, 1916, 475.

[12] W. P. Lass, *Met. and Chem Eng.*, 1915, **13**, 566; *J*, 1915, 1013.

[13] *Min. and Eng World*, 1916, **44**, 601; *J.*, 1916, 543

[14] *J. Chamber of Mines, W. Australia*, Feb. 1915; *J.*, 1915, 908

[15] *J. Chem., Met., and Min. Soc, S. Africa*, 1915, **15**, 322; *J.*, 1915, 964.

[16] *J. Chem., Met., and Min. Soc., S. Africa*, 1916, **17**, 87; *J.*, 1917, 220

gave good results. It was found that the middlings and tailings were directly amenable to cyanide treatment, and that after roasting the concentrates could be amalgamated and cyanided. The estimated extraction on a commercial scale was put at 81.

In connection with the treatment of West African graphitic schists, W. R. Feldtmann[17] has patented a method for dissolving gold by the use of sodium sulphide solution and precipitating the metal by means of metallic copper or copper sulphide.

SILVER

Most of the developments connected with the production of silver have been in the direction of increasing the efficiency of what may be termed recognized standard methods, such as amalgamation and cyaniding.

The tailings from high-grade silver ores left after amalgamation in strong cyanide solutions carry notable proportions of mercury which is chiefly in the form of sulphide. This can be recovered[18] by leaching the filter cakes with a solution containing 1% of sodium sulphide and 1% of sodium hydroxide, and precipitating the metal on aluminium in the form of foundry waste.

C. R. Morris[19] shows that in cyaniding sulphide ores the addition of lead acetate gives a slightly better extraction with fresh solutions, but a slightly lower one with mill solutions which contain zinc.

The difficulty of extracting silver by cyanide solution from the El Favor Mine ores when associated with manganese oxide[20] has been overcome by roasting such ores with 2½% of salt at a low temperature for about 15 minutes prior to leaching. The alternative method suggested is that of roasting the ore under reducing conditions, as when mixed with powdered coal.

It would appear that there are difficulties at the present time in obtaining aluminium powder for use as a precipitant.[21] As an alternative the silver may be precipitated by sodium sulphide solution and the sulphide precipitate treated with sodium hydroxide in the presence of aluminium ingots.

With reference to the treatment of the Cobalt district ores, at the Canadian Copper Co.'s Copper Cliff works[22] the ore is smelted and silver bullion, speiss, and slag thereby produced. The bullion, containing about 75 % of the total silver, is cupelled in an oil-fired cupellation furnace, whilst the speiss is given a chloridising roast and then leached with thiosulphate for the recovery of silver. This treatment does not completely remove the silver, so that the residues are again smelted and the speiss treated as before. The residues from the second treatment are dried, roasted with sodium nitrate and sodium carbonate, leached with water and finally with thiosulphate.

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[17] Eng. Pat 12654, 1914, *J*, 1915, 720

[18] E. B Thornhill, *Min and Eng. World*, 1915, **43**, 329; *J*, 1915, 1014

[19] *Eng and Min J.* 1915, **100**, 189; *J*, 1915, 908.

[20] W. Neal, *J. Chem Met. and Min. Soc, S. Africa*, 1916, **17**, 9; *J*, 1916, 1113.

[21] R. B. Watson, *Bull. Canadian Inst. Min. Eng*, Nov, 1916; *J.*, 1917, 459.

[22] R. W. Bridges, *Eng. and Min. J*, 1916, **101**, 646; *J*, 1916, 604.

Attention has been given to the influence of sulphates and sulphur dioxide on "spirting," and the prevention of this trouble as connected with castings. W. Stahl[23] describes a method of obtaining sound silver castings which is essentially a "poling" operation for de-oxidising the metal before it is poured.

MERCURY.

Recent progress in the metallurgy of mercury has been principally in the direction of wet concentration, the briquetting of the concentrates and fine ores, and the use of multiple-hearth roasting furnaces.

Wet concentration has become more general on account of the richer mercury ores becoming exhausted and the necessity of treating low grade material. There is still room for improvement in this direction.

Briquetting naturally follows concentration unless the entire output of concentrates is to be reduced by methods similar to those adopted for fine ores. Up to the present the difficulty has been to find a satisfactory binder which must be free from volatile hydrocarbons, otherwise considerable trouble is experienced in the collection of the metal.

According to W. H. Landers,[24] multiple-hearth roasting furnaces have scarcely passed the experimental stage, but he states that they have proved more economical than the Scott tile furnace, or furnaces of similar type, especially in fuel consumption.

LEAD.

The density of lead increases if the pure metal is suspended in a 40 % solution of lead acetate containing 100 c.c. of nitric acid (sp. gr. 1·16) per litre. Dilatometric measurements[25] lead to the view that the changed lead is made up of allotropic forms.

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[23] *Metall u. Erz*, 1916, **13**, 297; *J.*, 1916, 1263.

[24] *Eng. and Min. J.*, 1916, **102**, 630; *J.*, 1916, 1160.

[25] E. Cohen and W. D. Helderman, *Z. physik. Chem.*, 1915, **89**, 733; *J.*, 1915, 908.

There have been no striking changes during the last two years either in the preparation or the smelting of lead ores. Hand-roasting has been practically superseded by blast-roasting and sintering, and where the old style of roasting in a mechanically rabbled hearth is still in use, it is now generally followed by a finishing roast on a Dwight-Lloyd machine or in one of the types of blast-roasting pots.

A S Dwight[26] states that to bring the sulphur content in the roasted material down to 2 5 % the roasting operation should be carried out in two stages, initial and final.

No appreciable change has taken place in the design of blast furnaces, but improvements have been made in furnace working and economies effected in the handling of the charges. A modern rectangular furnace will smelt 200 to 250 tons of ore per day, using 10 % to 15 % of fuel when working at a blast pressure of 2 to 2½ lb. per square inch.

The influence of the shape of tuyere on the rate of smelting is shown by the results of experiments carried out at Cockle Creek Smelter, N S W[27] It was found that large diameter tuyères give better results than conical tuyères using air at the same blast pressure

Rich lead ores are still smelted by the Flintshire process, and it is interesting in this connection to note that a continuous furnace of the horizontal type for the treatment of this class of ore has been patented by C J Beaver and E A Claremont[28]

COPPER

A review of the output of copper in the various producing countries of the world is given in the *Engineering and Mining Journal*.[29] The consumption in the United Kingdom in 1913 was 140,300 tons, the amount produced in metallurgical works 52,100 tons, whilst the output of mines was only 300 tons

With reference to the mechanical properties it has been found that these are improved by the addition of nickel to the metal, which causes an increase in both the tensile strength and the percentage elongation.[30] L Guillet[31] has investigated the effect of cold working, and reports that there is no relationship between the hardness and the tensile strength of worked metal

Whilst there have been no striking developments in pyrite smelting during the past two years, much valuable information can be obtained from R. C. Sticht's review[32] of the Mount Lyell practice. According to H. O. Hofman,[33] partial pyrite smelting is now generally adopted in America and coke-smelting of roasted copper ores is being abandoned. Considerable attention has been given to the collection and treatment of flue dust and fume, and in place of briquetting these materials the method of mixing with converter slag or agglomerating by blast roasting is being adopted.

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[26] *Eng and Min J*, 1916, **102**, 671 ; *J*, 1916, 1159

[27] A W. Tournay-Hinde, *Eng. and Min J*, 1916, **102**, 392 ; *J*, 1916, 968

[28] Eng Pat 6675, 1915 , *J* , 1915, 1150.

[29] *J*, 1917, 74

[30] W Stahl, *Metall u. Erz*, 1915, **12**, 179 , *J* , 1916, 52.

[31] *Rev Mét* , 1915, **12**, 819 ; *J* , 1916, 311

In reverberatory furnace practice considerable developments in the methods of firing have taken place. Oil and coal dust firing is now becoming common, as it avoids loss of heat in the fire box. A typical example is to be found at Anaconda, where a furnace 147 feet by 25 feet is fired with coal dust.

In converter practice acid linings have been almost entirely superseded by basic linings, and in this connection the proposal of J. B. F. Herreshoff[34] to use refinery slag as silicious material in the converter, is interesting.

Blast-furnace treatment of copper-gold ores has been adopted at Mt. Morgan,[35] Queensland, in preference to reverberatory furnace treatment, on account of working considerations, and not on account of the slight differences shown in profits.

F. E. Lathe[36] deals with the question of metal losses in copper slags, and the general conclusion arrived at is that sulphide and oxide exist at the same time in these furnace products. Investigations carried out at the works of the Granby Consolidated Mining, Smelting and Power Co., Ltd., Grand Forks, B.C., have shown that by deepening the blast furnaces and employing a series of settlers for the slag the copper content of the latter can be materially reduced. The proposal for reducing the loss of oxidised copper in slags, by providing the reverberatory furnace near the skimming end with a wall sufficiently low to allow the slag to run over, and yet keep back the matte, and by adding pyrites to the slag separated, is regarded as promising.

Progress in the hydro-metallurgy of copper has been very largely confined to modifications of what might be termed standard methods. It is stated by S. Barth,[37] for example, that the roasting of cupriferous pyrites can be carried out in the Bracq-Moritz furnace so that 87 % of the total copper in the roasted material is in a soluble form.

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[32] *Proc. Austral. Inst. Min. Eng*, 1915, **19**, 75; *J*, 1916, 118

[33] *J. Franklin Inst.*, 1916, **181**, 83; *J.*, 1916, 257

[34] Eng. Pat. 2219, 1915; *J.*, 1915, 803.

[35] B. Magnus, *Eng. and Min. J.*, 1916, **102**, 668; *J.*, 1916, 1159.

[36] *Eng. and Min. J.*, 1915, **100**, 215; *J*, 1915, 1014.

[37] *Chem. Apparatur*, 1915, **2**, 95, 105; *J.*, 1915, 1149.

A 2000-ton leaching plant[38] was completed at Anaconda in May, 1913, for working up a dump of twenty million tons of tailings containing 0·64% copper and 0·18 oz. silver per ton. The material is first given an oxidising roast at a low temperature in furnaces of the McDougall type, then leached with three solutions containing varying proportions of sulphuric acid and salt, and finally washed with water. Copper and silver are recovered from the solutions by means of iron. The total extraction averages 80% of the copper and 60% of the silver.

The treatment of slime containing about 1% copper resulting from the rough concentration of the ore of the Burro Mountain Copper Co., as arranged by J. Douglas,[39] consists of four essential stages, de-watering, roasting, leaching, and electrolysing. The water content is first reduced to 30% by settling, then brought down to 10% by exposing to air in shallow pans, and finally to 1% by passing through an oil fired rotary drier. After disintegration it is passed to a six-hearth McDougall furnace, in the third hearth of which fuel oil is burnt so as to maintain a maximum temperature of 510° C. The hot roasted product is then delivered into a long, inclined, rectangular trough containing dilute sulphuric acid of 3½% strength, and from this to seven Dorr thickeners. The copper is finally recovered by electrolysis of the sulphate solution.

The recovery of copper in burnt pyrites is effected at Pernau[40] by roasting with salt according to the Buddeus[41] process, which employs compressed air. The treatment of low-grade carbonate ores with a solution of aluminium sulphate[42] will no doubt extract copper, but a great deal depends in processes of this description on the cost of regenerating or producing the solvent.

ZINC

At the beginning of the war the position of the zinc industry in this country could not be considered as altogether satisfactory, but it is gratifying to note that the Government have arranged to take at least 100,000 tons of Australian concentrates in 10 years and up to 4,500 tons per annum of the spelter produced in Australia over the same period.

The development of the spelter industry is set out very fully by E. A. Smith.[43] J. C. Moulden's paper on "Zinc, its production and industrial application," read before the Society of Arts, in May, 1916,[44] should also be consulted. Progress in the metallurgy of this metal has been principally in the direction of obtaining improved extraction and reduction of labour costs chiefly by the use of gas-fired furnaces, worked on the regenerative system. Electric smelting, however, has passed the experimental stage, and has been proved to be of commercial value. In the Côte and Pierron process blende is smelted in an electric furnace without a preliminary roast and lead is recovered at the same time.

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[38] F. Laist and H. W. Aldrich, *Min. and Eng. World*, 1916, **8**, 321; *J.*, 1916, 1019.

[39] See L. Addicks, *Met. and Chem. Eng.*, 1915, **13**, 531; *J.*, 1915, 1014.

[40] *Metall u. Erz*, 1915, **12**, 379.

[41] Ger. Pat. 285888; *J.*, 1915, 1150.

[42] J. Erdös, Eng. Pat. 4658, 1914; *J.*, 1915, 875.

[43] *J. Inst. of Metals*, 1916, **16**, 118–174. See *J.*, 1916, 996.

According to the method worked out in the University of Utah,[45] it is possible to remove iron sulphide from very pyritic zinc ores by treating in a reducing atmosphere at 600° C. and then leaching with dilute sulphuric acid.

The Hegeler mechanical roasting furnace is stated by M. de Lummen[46] to be employed almost exclusively in the United States, where labour is expensive and fuel cheap. He also states that of the mechanical furnaces tested in Europe during recent years for blende roasting, the de Spirlet type has given the most promising results.

The Roitzheim-Remy continuous distillation process[47] is a distinct development in the treatment of the roasted ore. This process consists of feeding the pre-heated charge into the top of a vertical gas-fired retort and mechanically discharging the residue from the bottom in such a way that the open ends of the retort are sealed to the air. The advantages claimed for the process are a considerable reduction of labour, reduced consumption of refractories, and a general saving in costs. In a somewhat similar process patented by J. M. Hyde[48] the roasted ore mixed with the reducing agent is fed into an inclined retort, the zinc vapour collected in an external condenser, and the hot residue mixed with fluxes and smelted for the recovery of other values.

The majority of the wet processes are now associated with the production of electrolytic zinc, which is dealt with in another section of this volume. A modification of the bisulphite process[49] consists of treating the roasted ore with zinc bisulphite solution whereby sulphite is formed which is afterwards converted into bisulphite by sulphur dioxide.

Several patents have been taken out for reducing the oxide under electrically heated conditions. A patent by W. M. Johnson and others[50] specifies that the roasted ore shall be heated with carbon to 1150 C in muffle retorts and the residue treated with additional carbon under electrically heated conditions, but according to F. W. Highfield[51] the oxidised material is fed on to electrically heated carbon after treatment with carbon monoxide.

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[44] *J. Roy. Soc. Arts*, 1916.

[45] *Min and Eng World*, 1916, **45**, 987 ; *J*, 1917, 35.

[46] *Chem. Trade J*, 1916, **58**, 255 ; *J*, 1916, 425.

[47] M Liebig, *Metallu Erz*, 1916, **13**, 143 ; *J*, 1916, 846

[48] U S. Pat. 1144037, 1915 ; *J*, 1915, 837.

[49] Fr. Pat. 474306, 1914 ; *J*, 1915, 803.

[50] U.S. Pat. 1165371, 1915 ; *J*, 1916, 259.

The purification of common spelter has received considerable attention, and W R Ingalls[52] states that by redistilling with proper control of the temperature and separation of the first distillate, a high grade spelter low in cadmium, can be produced

According to F Juretzka,[53] electrically heated furnaces are much more advantageous for the re-distillation of spelter, and provided the distillation is carried out at a low temperature there is no difficulty in obtaining spelter containing 99·7 to 99·9 % of zinc.

Gallium has been found in small quantity in the zinc-lead dross remaining from the distillation of spelter[54] It appears in the form of drops, resembling mercury, on the surface of the dross after this has been exposed to the weather for some time.

TIN

The important problem of the present day as far as tin is concerned is the saving of values in the slimes produced in concentration Research work in this connection has been entrusted to the Institution of Mining and Metallurgy by the Privy Council Research Committee, but up to the present no results have been published

There has been little, if any, alteration in the methods employed for the reduction of tin concentrates It is true, however, that numerous patents have been taken out for the recovery of the metal from this class of material and some may lead to valuable practical results

The treatment of sulphide tin ores has always been an interesting problem. The following methods have been tried and have resulted in partial success (1) reverberatory furnace smelting in the presence of iron or carbon; (2) pyritic smelting, (3) blast-roasting, followed by ordinary blast-furnace smelting. J H. Levings[55] proposes to treat these ores by blast-furnace smelting, after blast-roasting, and then treating the copper-tin alloy and matte formed in such a way as to produce a silver-copper bullion and tin oxide, which is volatilized.

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[51] Eng Pat 6865, 1914; *J*, 1915, 838

[52] *J Inst of Metals*, 1916, **16**, 196-199; *J.*, 1916, 1020

[53] *Chem.-Zeit.*, 1916, **40**, 885; *J*, 1916, 1263.

[54] W. F. Hillebrand and J. A. Scherrer, *J. Ind. Eng Chem*, 1916, **8**, 225; *J*, 1916, 473.

[55] *Proc Austral Inst. Min. Eng*, 1915, **19**, 183; *J*, 1916, 119

ALUMINIUM.

The ever-increasing demand for light alloys, especially for aeronautical work, and the advisability of substituting a satisfactory metal or alloy for copper wherever possible, has given a great impetus to the aluminium industry.

The use of aluminium for electrical purpose is fully dealt with by E. V. Pannel,[56] who states that owing to aluminium alloys tending to deteriorate in use they are not to be recommended for electrical purposes. Pure aluminium rods are being used, however, quiet satisfactorily as conductors in accumulator stations and elsewhere.

In view of the extended use of light alloys mentioned above, the results of H. Schirmeister's[57] investigations with reference to the influence of the common metals on the properties of aluminium, are important.

Considerable attention has been devoted to the jointing of the pure metal and its alloys. According to Pannel,[56] permanent union of aluminium surfaces is only attainable by autogenous welding with or without the use of an alkali sulphate or fluoride as a flux. Solders, however, are still employed, the composition of which varies considerably as shown by the following patent specifications. —

	Tin.	Lead	Aluminium.	Zinc	Phosphorus
(*a*)[58]	80	16	8	16	8
(*b*)[59]	12·8	3·2	1	--	—

The treatment of pot-skimmings, turnings, etc, for the recovery of the metal is a problem that will have to be seriously faced, but up to the present patents, relating thereto do not show much of a novel character.

The production of aluminium is essentially an electro-metallurgical problem (see p. 292).

ALLOYS.

The amount of information available on this subject is so extensive that it is only possible in a report of this character to give the briefest *resume* of developments during the past two years.

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[56] Amer Inst. of Metals, Sept., 1915; *J*, 1915, 1058

[57] *Stahl u Eisen*, 1915, **35**, 648, 873, 996.

[58] J. F. Gross, U S. Pat. 1145307, 1915; *J*, 1915, 875

[59] J. Cayocca, U.S. Pat. 1161612, 1915; *J*, 1916, 54.

C. R. Barton[60] gives a full account of the manufacture of cartridge brass (70/30) the total impurity in which must be less than 0·4 %, but arsenic, antimony, lead, and cadmium must be below 0·08 %.

The influence of arsenic on brass has been investigated by O. Smalley.[61] The general conclusions are that arsenic embrittles all Cu-Zn alloys when it is present as free arsenide, but the arsenide films do not affect the cold working properties of α-brasses to any appreciable extent, whereas it is detrimental, even when present in the most minute quantities, to the physical properties of hot-worked brass without affecting the hot working properties. The annealing of arsenical brass is dealt with by C. H. Mathewson and M. Thalheimer.[62] According to P. D. Merica and R. W. Woodward[63] initial stresses in brasses vary in distribution and magnitude, the outside layers of extruded and forged rods being under compression and of wire-drawn rods in tension.

The presence of initial stresses of large magnitude results in failures by fracture or fissure. Valuable contributions to the subject of brasses and bronzes were made by O. F. Hudson and R M Jones, D. Meneghini, C. H. Desch and H. Hyman, and W. B. Parker, at the autumn meeting of the Institute of Metals,[64] 1915, on the constitution of ternary brasses, structural changes in industrial brasses, the corrosion of gun-metal and brasses, and the value of phosphor bronze for high-speed superheated steam turbine blades.

The third report of the Corrosion Committee was presented at the 1916 Spring Meeting[65] and dealt with experiments on hard drawn and annealed tubes of 70/30 brass, Admiralty metal, phosphor-bronze, aluminium-copper, etc. None of the alloys tested proved entirely satisfactory. At the same meeting A. Stansfield gave a comprehensive summary of the use of electric furnaces in non-ferrous metallurgy, F. C. Thompson a paper on the effect of heat treatment on a series of Cu-Ni-Zn alloys, and W. H. Withey a paper on the analysis of aluminium and its alloys, whilst A. A. Read and R. H. Greaves showed from their study of the ternary alloys of Cu-Al-Sn that no advantage is gained by substituting aluminium for tin in gun-metal.

The Annual General Meeting, 1917, of the same Institute[66] was devoted principally to a general discussion on the melting of non-ferrous metals (see also section on Fuel, pages 36 seq.). It appeared from this discussion that gas-fired furnaces, whether using high or low pressure gas, have the advantage over coke-fired furnaces, although the latter are more largely employed than any other type.

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[60] *Eng. and Min J*, 1916, **101**, 97; *J*, 1916, 740

[61] *J.*, 1917, **36**, 429.

[62] *J. Inst. of Metals*, 1916, **16**, 18; *J.*, 1916, 1064.

[63] *J. Franklin Inst.*, 1916, **182**, 803; *J.*, 1917, 140.

[64] *J. Inst. of Metals*, 1915, **14**; *J.*, 1915, 1015.

[65] *J. Inst. of Metals*, 1916, **15**; *J.*, 1916, 472, 473.

[66] *J. Inst. of Metals*, 1917, **17**; *J.*, 1917, 321-325.

Blemishes formed on the surfaces of rolled brass during annealing have been traced[67] to mineral matter arising from the soaps in the lubricating greases used in rolling. The paper by H. W. Brownsdon[68] on the use of nitre cake in the preparation of pickling solutions for brasses is important in view of the difficulty of obtaining the acid supplies required.

The heat treatment of 10 % aluminium bronzes has been investigated by A. Portevin and G. Arnou.[69] The two alloys tested were similar in composition except that one contained 1 % of manganese, and records were made of the influence of varying the quenching temperature and reheating after quenching from 800° C. and 900° C.

An exhaustive examination of the Al-Zn alloys has been made by O. Bauer and O. Vogel,[70] who devoted considerable attention to the corrosion of this series of alloys. They found that if such alloys were immersed in a solution of potassium carbonate, sodium bicarbonate, and potassium bichromate at a suitable temperature, a coating was formed which resisted the action of tap water and sea water.

Systematic investigation of the gold-copper alloys by N. Kurnakov and others[71] has revealed several interesting points especially in connection with the heat treatment, rolling, and wire-drawing of alloys of certain composition.

The control of platinum has given considerable impetus to the use of the alloys of Pd-Au and Pd-Ag. According to F. A. Fahrenwald,[72] tungsten and molybdenum can be substituted for platinum-iridium.

C. H. Tonamy[73] has shown that X-rays can be used for the detection of blowholes in metal castings, and by taking radiographs in two directions at right angles the depth of a blowhole beneath the surface can be determined. This was confirmed almost simultaneously by W. P. Davey,[74] who has given a useful exposure formula which involves the thickness of the metal.

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[67] *Rev. Mét.*, 1915, **12**, 101

[68] *J*, 1917, **36**, 575.

[69] *Rev. Mét.*, 1916, **13**, 101 ; *J*, 1916, 1114.

[70] *Mitt k Materialpruf.*, 1915, **33**, 146 ; *J.*, 1916, 543.

[71] *J. Russ. Phys Chem. Soc*, 1915, **47**, 871 ; *J*, 1915, 1254.

[72] *Min. and Eng. World*, 1916, **44**, 606 ; *J*, 1916, 543

[73] *J. Inst. of Metals*, 1915, **14**, 200 ; *J.*, 1915, 1016.

[74] *Trans. Amer. Electrochem. Soc*, 1915, **28**, 407 ; *J*, 1915, 1095.

CONCENTRATION.

There is still a divergence of opinion as to whether this subject belongs to the domain of the metallurgical or mining engineer, and therefore it is not proposed to do more than refer to the extent of the work carried out. In the United States[75] there are probably 200 ore flotation plants in operation using a variety of oils according to the class of ore treated. Differential flotation of such sulphides as galena and blende is now possible, if the numerous patents taken out recently can be accepted as a guide, and the difficulty of treating oxidised ores by this process is not insurmountable provided such ores are given a preliminary treatment with a sulphur compound.

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[75] R J Anderson, *Met and Chem Eng*, 1916, **14**, 135, *J*, 1916, 312

ELECTRO-CHEMISTRY.

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In reviewing the progress of electro-chemistry during the past three years, no one special line of advance can be easily distinguished. Healthy and steady development, as a whole, has characterised the progress of the last few years. Electro-chemistry, besides possessing special spheres of its own, has penetrated into practically every branch of chemistry and compelled the recognition of its general utility.

DEVELOPMENT OF POWER AND PLANT.

Increased utilisation of the world's water powers is reported. In Norway,[1] extension has been applied to the production of aluminium, carbide, and cyanamide. In South Africa, the development of water power is to be utilised for production of materials for agriculture and mining, carbide, cyanide, cyanamide, and ammonia, with power at an estimated cost of 0·2d. per unit, and in the event of the cost falling below this figure, direct nitrogen fixation and electric steel making will be developed.[2]

A large power scheme is in operation in Tasmania[3] the main water storage being the Great Lake. The present output is 10,000 h.p., but this may be increased to 25,000 h.p. or more. The minimum charge has been fixed at £2 per h.p. year (about 0·08d. per unit). Most of the power is to be used for zinc production (electro-metallurgical and electrolytic), caustic soda and bleaching powder, carbide, steel, ferro-alloys, and cement making. It is also proposed to manufacture aluminium, nitric acid, and per-salts.

In a paper dealing with electro-chemical plant,[4] the great importance of low-voltage machines of high capacity is emphasised, as well as the value of the contrivances now used for variation of voltage in electro-chemical work, such as "booster" control. The perfecting of induction regulator control now provides converters in which considerable voltage variation is possible.

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[1] *Engineering*, 1915, **100**, 673.

[2] *Report S African Inst. E Engineers*, Jan 1916 ; *J*, 1916, 896.

[3] *Proc. Soc Chem Ind Victoria*, 1916, 419 ; *J.*, 1916, 1265.

[4] J L Yardley, Amer. Elect. Soc, Oct. 1917 ; *J.*, 1917, 1182.

PRIMARY CELLS. DEPOLARISERS. SECONDARY CELLS.

During the past three years most of the work in connection with primary cells has been devoted to the improvement of the Leclanché dry cell by increasing the efficiency of the depolariser, by adding new ingredients to the electrolyte, or by introducing an absorbent material in the make-up of the cell

A few primary cells of new design have been announced For example, in one, carbon forms the positive plate in a solution of hydrobromic or hydriodic acid mixed with sulphuric acid, the negative plate is likewise of carbon and is immersed in a solution of nitric or chromic acid, and sulphurous acid or other reducing agent is present in the liquid to regenerate acid from the halogen liberated in the positive compartment.[5]

In another cell the negative plate is of tin coated on one side with a layer of sulphur, so that a sulphide of the positive metal (zinc) is formed during action. The electrolyte is a solution of alkali or alkaline-earth chlorides and the precipitated zinc sulphide may be collected.[6] In two cells which contain an alkaline electrolyte, and zinc anode plates, one has potash for electrolyte and a negative plate of graphite and mercuric oxide[7]; in the other, alkali zincate is mixed with the alkaline electrolyte.[8]

As regards the addition of absorbents to ordinary dry cells, according to one patent[9] the carbon and zinc are separated by porous material such as cotton wool mixed with ammonium chloride, and a piece of absorbent material saturated with zinc chloride is placed next the inner electrode.

In another process,[10] the container is made of pulp reinforced by an embedded metal winding, inside the container is the zinc plate and next to this a layer of absorbent material saturated with aluminium chloride and a filler including mercury salts. The electrolyte is made up of glycerin, gelatin, and ammonium, aluminium, and zinc chlorides

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[5] Eng. Pat 112 (1915); *J*, 1916, 125

[6] Eng. Pat 103020 (1916); *J*, 1917, 295

[7] Eng Pat 9684 (1915); *J*, 1916, 897

[8] Eng Pat 16471 (1915), *J*, 1916, 1068

[9] Eng Pat. 18713 (1914); *J*, 1915, 732

[10] U.S Pat. 1140826 (1915); *J*, 1915, 722

Specially prepared manganese peroxide, as depolariser, is the subject of numerous patents. In some cases it is prepared from permanganate by the reducing action of a manganous salt[11] or an organic substance,[12] or the peroxide is improved by incorporating with it oxidising agents such as mercuric oxide or a persulphate.[13]

It has been shown that the amount of chemical change in small pocket-lamp batteries is about twice that due to current given and represents losses by local action owing to impurities.[14] Leclanché cells may be revived, when exhausted, by moistening the material of the porous pot with hydrochloric acid, and for this purpose a funnel-shaped opening may be provided, passing through the pitch to the interior.[15] A similar method of regenerating the electrolyte and depolariser is the subject of another patent.[16]

The cadmium standard cell can be improved by using calomel as depolariser instead of mercurous sulphate in the usual arrangement $Hg/Hg_2Cl_2/CdCl_2/Cd$ amalgam. The cell was found to give a constant voltage at 25° C. of 0·67079 to 0·67080 volt over a long period of time, and showed no tendency to gradual decrease of E M.F. as is often noticed with the ordinary Weston cell. The temperature coefficient at 18° C. with a saturated solution is 0·000067 volt[17]

Secondary cells have received some attention, chiefly with a view to improve the plates used, but also with a view to cure sulphating. Negative plates after being "formed" can be treated with a solution of alkaline-earth persulphate[18] to oxidise the lead, and the resulting calcium or barium sulphate fills the interstices of the surface but does not interfere with "charging" or "discharging" In another process, battery paste for the plates is made up of twenty-five parts of lead oxides, one part each of glycerin and water, and 0·5 part of sulphuric acid. This paste is heated to dryness at 120°–140° C. and mixed with sulphuric acid and water.[19] The plates of accumulators can be built up from a central core of lead-antimony alloy from which parallel ribs extend on either side; the ribs are of lead and are pocket-shaped to receive the active material.[20]

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[11] U S. Pat. 1184854 (1916); *J.*, 1916, 745; U.S. Pat. 1216450.

[12] U.S Pat. 1169943 (1916); *J*, 1916, 547.

[13] U.S Pat 1195677 (1916); *J*, 1916, 1068; U.S. Pat. 1147753 (1915); *J.*, 1915, 912

[14] K Arndt., *Chem -Zeit*, 1916, **40**, 1017; *J*, 1917, 89.

[15] Eng. Pat 11511 (1915); *J*, 1916, 476.

[16] U.S. Pat. 1192061 (1916); *J.*, 1916, 931.

[17] Lipscomb and Hulett, *J. Amer. Chem. Soc.* 1916, **38**, 20; *J.*, 1916, 261.

[18] U.S. Pat. 1164464 (1915); *J.*, 1916, 186.

[19] Eng. Pat. 9012 (1915); *J.*, 1916, 851.

[20] U.S. Pat. 1190982 (1916); *J.*, 1916, 987.

To regenerate "sulphated" storage cells, charging and discharging with an electrolyte of acid sodium sulphate is recommended.[21] A low current density is used at first and progressively increased. It is stated that "sulphating" may be cured by long soaking of the plates in sodium sulphate solution.[22]

Materials suitable for separating accumulator plates are still being devised. One of these is composed of acid-resisting material such as asbestos mixed with a finely divided soluble substance and a phenol-condensation product like "Bakelite", the mixture is moulded and baked, after which the soluble matter is washed away.[23] Another separator is of wood treated with baryta or strontia solution, these bases being then converted into insoluble sulphates.[24]

A contribution to the theory of the lead accumulator has been given by C. Féry,[25] in which the discharge is compared with that of a galvanic cell, with a solid depolariser, the difference being that in the accumulator an insoluble salt is formed on the negative plate. The theory of "double sulphating" is stated to be incorrect and the following equations are given to represent normal "discharge":

$$Pb + H_2SO_4 + Pb_3O_7 = PbSO_4 + H_2O + 3\ PbO_2.$$
$$Pb + H_2SO_4 + Pb_2O_5 = PbSO_4 + H_2O + 2\ PbO_2.$$

These equations agree with the formation of 12.11 grms. of higher oxide per ampere-hour. The amount of acid combined during "discharge" is one-half that required by the double-sulphating theory and the variations in the mass of the positive plate are small and in the opposite sense to that demanded by the theory.

The alkaline storage battery has received attention chiefly in order to improve the plates. The positive plate may be a perforated tubular receptacle of conducting material packed with nickel oxide and ceric oxide, while the negative plate consists of iron or iron compounds easily oxidised contained in nickel tubes.[26] A negative plate for alkaline batteries is composed of an insoluble zinc-titanium compound, obtained by making a paste of zinc salt, sodium titanate, and mercury compound, and then reducing it by electrolysis.[27]

In another cell the electrodes are of manganese dioxide and lower oxides of manganese respectively, the electrolyte being an alkaline solution of potassium nitrate.[28] The positive plate of another cell is made with lithia and nickel oxide mixed with carbon.[29] An alkaline storage cell devised by L. C. Turnock[30] has positive plates of nickel hydroxide and the negative plates are of pure metallic iron mixed with a small quantity of mercuric oxide; the electrolyte is 21 % potash containing 50 grms. of lithia per litre.

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[21] U.S. Pat. 1147261 (1915); *J.*, 1915, 912.

[22] Perley and Davis, *J. Phys. Chem.* 1916, **20**, 164; *J.*, 1916, 315.

[23] U.S. Pat. 1206983 (1916); *J.*, 1917, 146.

[24] U.S. Pats. 1228368, 1228369 (1917); *J.*, 1917, 891.

[25] *Amer. J. Sci.*, 1916, **42**, 366; *J.*, 1916, 1119.

[26] U.S. Pat. 1167485 (1916); *J.*, 1916, 485.

[27] U.S. Pat. 1139213 (1915); *J.*, 1915, 667.

The carbon cell of Hofmann and Ritter[31] appears to be a true carbon cell since in it electrical energy is liberated by the oxidation of carbon to carbon dioxide. It is therefore different from the cell of Jacques (*J.* 1904, 940), and consists of platinum immersed in hypochlorite solution and carbon immersed in caustic soda; it may be regarded as an oxygen-concentration cell with a carbon depolariser; the voltage given is 0·76–0·91 volt. The cell is really a semi-electrochemical oxidation and reduction cell since the depolarising action of the carbon is chemical. In the same paper an iodoform cell with an E.M.F. of 0·27 volt and a nitrobenzene cell with an E.M.F. of 1·1 volt are described.

Two examples of photo-chemical cells have been reported by T. W. Case. In the first experiments,[32] in which two copper plates were immersed in sodium chloride solution and connected by a wire externally, it was found that on exposing one to light while the other was protected, an E.M.F. of 0·1 volt developed and a current of 0·2 ampere. Subsequently it has been found[33] that certain electrolytes (copper formate containing formic acid) deposit on the metal a photo-sensitive layer, and on coupling such plates and exposing one to light a current is produced. It seems possible to develop along these lines a cell capable of converting light energy into electrical energy.

ELECTRODES AND ELECTROLYSIS.

Several processes have been patented for rendering electrodes of pyrolusite, magnetite, or graphite more permanent and efficient. Pyrolusite may be first purified by treatment with sulphuric acid, and after being moistened with manganese nitrate the substance is moulded into the desired shape.[34] By repeatedly soaking in manganese nitrate and subsequent ignition a dense and hard electrode may be obtained. Magnetite electrodes may be rendered less brittle by incorporation of cupric oxide,[35] and an electrode of fused ferric oxide is recommended as a bipolar in the manufacture of chlorates.[36] An anode for use in sulphate solutions is composed of iron and lead oxides fused in the right proportion to give a composition agreeing approximately with the formula $Fe_2O_3,7PbO$.[37]

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[28] Ger. Pat. 294860 (1914); *J.*, 1917, 90.

[29] Fr. Pat. 477623 (1914); *J.*, 1916, 608.

[30] *Met. & Chem. Eng.*, 1916, **15**, 259; *J.*, 1916, 1023.

[31] *Z. Elektrochem.*, 1915, **21**, 325; *J.*, 1915, 1101.

[32] *New York Elect. Soc.*, June, 1916; *J.*, 1916, 1023.

[33] *Amer. Electrochem. Soc.*, May, 1917; *J.*, 1917, 1102.

[34] Ger. Pat. 282225 (1914); U.S. Pat. 1143828 (1915); *J.*, 1915, 622, 839.

The resistance of carbon electrodes may be diminished by intermixture of metal powders, such as copper, aluminium, etc., or salts or oxides of these which will yield the metals during the ignition of the electrode.[38] Graphite electrodes can be made by using graphitic acid as a binding material and subsequently heating to the temperature of decomposition.[39]

To prevent the disintegration of graphite anodes during the electrolysis of copper liquors, sufficient ferrous sulphate and sulphurous acid should be kept near to it, in order to prevent evolution of oxygen.[40]

Copper oxide makes a suitable negative electrode. The oxide is maintained at fusion temperature till an intimate mixture of cupric and cuprous oxides is obtained in the ratio of 1 : 2; this is then moulded to the desired shape.[41] Such an electrode may be given a protective surface of copper which is amalgamated with mercury.[42]

Economy of platinum results from using aluminium as a support for platinum gauze; a reliable electrode of large surface is thus formed and no corrosion takes place where the two metals are in contact.[43] Another form of metal electrode which aims at economy of material, and which is suitable for giving high current density, is made of wires which hang in the bath and which may be weighted to keep them straight.[44]

Alternating current is being increasingly used in conjunction with direct current for electrolytic processes. Its main function appears to be to keep the electrodes "clean," as in Wohlwill's improved gold-refining process. Materials which would otherwise adhere to the electrode are prevented from thus impairing its efficiency by being continually shaken off by the rapid changes of pressure which the alternating current produces at the electrode surface.[45]

In electrolytic measurements which depend in part or entirely upon the contact of a metal with an electrolyte (contact difference of potential) it is essential that the character of the metal used shall be always the same, and the reproducibility of metal electrodes has been investigated recently on several occasions. Thus, in working with copper, F. H. Getman[46] has found that spongy copper on platinum is the only invariable form. He has found also that spongy cadmium is not reproducible, but that cadmium sticks which had turned grey in a solution of the iodide gave constant results. Lead electrolytically deposited on platinum also gives a reproducible electrode.

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[35] *Amer Electrochem Soc*, May, 1917, *J*, 1917, 1102

[36] Ger Pat 281511 (1913); *J*, 1915, 559

[37] Ger Pat 278038 (1913); *J*, 1915, 236

[38] Fr Pat 480803 (1915), *J*, 1917, 146

[39] Ger Pat 282108 (1914); *J*, 1915, 668

[40] U S Pat 1193741 (1916), *J*, 1916, 971

[41] U S. Pat 1129818 (1915); *J*, 1915, 366

[42] U S Pat 1211388 (1917), *J*, 1917, 295

[43] Ger Pat 295178 (1914); *J*. 1917, 224

[44] U S. Pat 1209710 (1916), *J*., 1917, 146.

[45] J. C. Ghosh; *J Amer. Chem Soc*, 1915, **37**, 733; *J*, 1915, 559

A connection has been demonstrated between electrolytic and pure chemical processes by Reichenstein, who has recently published several papers on the subject which deal chiefly with the passivity of metals and the velocity with which metals are corroded by various solutions.[47]

Some interesting results have been obtained by the electrolysis of solutions of nitric, sulphuric, and phosphoric acids, using platinum cathodes and gold anodes. The gold is attacked in all cases forming auri-nitric acid in the first case and mixtures of hydrated aurous and auric oxides in the last two cases.[48]

When the current density on a cathode immersed in various aqueous electrolytes is increased sufficiently the cathode becomes red hot and may even melt. Experiments have been conducted with a thin sheet iron cathode in dilute sulphuric acid, and it is suggested that the intense heat effect might be used for the surface-hardening of steel objects and for alloying a metal surface with another deposited thereon.[49]

ELECTRO-OSMOSIS COLLOIDS

The behaviour of colloidal particles under the influence of a potential difference and the separation of these from one another and from crystalloids, form the subject of numerous patents during recent years. In one of the simplest cases the coagulation of colloids is brought about by causing them to lose the charges of electricity which they carry; thus, by inserting electrodes in the chambers of a filter-press the filtration is facilitated by the coagulation of the colloids, which are thus prevented from blocking the filter-cloth.[50] For the separation of the constituents of glue and gelatin, the solution is placed between diaphragms and subjected to an electric current which causes mineral ions to migrate through the diaphragms, the albuminoid material becomes coagulated and may be filtered off.[51]

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[46] *Trans. Amer. Elect. Soc.*, 1914, **26**, 67; *J.*, 1915, 365; *J. Amer. Chem. Soc.*, 1915, **37**, 953; *J.*, 1915, 622.

[47] *Z. Elektrochem.*, 1914, **20**, 406; **21**, 359; *J.*, 1915, 663, 1098.

[48] *Trans. Farad. Soc.*, 1916, **11**, 172; *J.*, 1915, 1100.

[49] C. Hering, *Met. & Chem. Eng.*, 1916, **15**, 454; *J.*, 1916, 1162.

[50] F. Ulzer, *Z. angew. Chem.*, 1915, **28**, 1, 308; *J.*, 1916, 575.

The process has been applied by the Gesellschaft für Elektro-Osmose to the tanning of skins.[52] The skin is placed between suitable diaphragms selected so that deleterious substances can pass away, but the active constituents essential to tanning cannot. The hide is charged positively or negatively and the tanning colloids move towards it in virtue of its charge and are thus brought into close contact. The same firm has patented a process for separating various colloids from each other,[53] which depends upon the use of diaphragms at different potentials. Non-sugars can be separated from crude sugar solutions and a solution of glue can be divided into several fractions.

An important paper dealing with this subject and its technical applications has been given by W. C. McC. Lewis[54] entitled "Some Technical Applications of Capillary and Electro-Capillary Chemistry."

Colloidal carbon has been obtained by passing an arc through various organic liquids in an ice-cooled flask. A green or red-brown solution was obtained which was very stable and showed the Tyndall effect. The final products of decomposition were carbon, chlorine, and hexachlorobenzene.[55] The addition of colloids (gelatin) to electroplating solutions has long been used to produce a good deposit. The effect was first thought to be due to "reducing action," then later it was ascribed to the "protective" action of the colloids; now, from a study of the behaviour of electrolysed solutions of silver nitrate and gelatin,[56] it seems that the colloid combines with the anions in the solution, reducing their velocity. When this velocity has been reduced to zero, the cations must carry the full charge, migrate as fast as they deposit on the cathode, and give a smooth deposit.

From a study of colloidal platinum and gold,[57] formed by the arc process, the former was found to be more stable than the latter. Stability was found to increase by the addition of certain ions (Cl, Br, I). Other evidence indicates that a certain critical potential difference at the surface of the particles determines the stability or instability of a colloidal solution.[58]

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[51] Eng. Pat. 21448 (1914); *J.*, 1915, 971.

[52] Eng. Pat. 19849 (1914); *J.*, 1915, 1020.

[53] Eng. Pat. 11823 (1914); *J.*, 1915, 877. Ger. Pat. 295666 (1915); *J.*, 1917, 295. Ger. Pat. 294667 (1915); *J.*, 1917, 377.

[54] *J.*, 1916, 575.

[55] *Z. Elektrochem.*, 1916, **22**, 252; *J.*, 1916, 889.

[56] ***Met. & Chem. Eng.***, 1915, **13**, **353**; *J.*, 1915, 721.

[57] ***J. Amer. Chem. Soc.***, 1915, **37**, 2667; *J.*, 1916, 52.

[58] **F. Powis**, *Trans. Chem. Soc.*, 1916, **109**, **734**; *J.*, 1916, 1015.

CONDUCTIVITY.

Conductors of aluminium, iron, and zinc have apparently come into general use in Germany during the war. A layer of oxide is a sufficiently good insulator for field-magnet windings in low-voltage machines and allows economy of space. As regards efficiency, compared with that of copper, aluminium is 1–2 % less, zinc 3–6 % less, and iron 8–12 % less. The price of aluminium being slightly lower than that of copper renders it, on the whole, a very good substitute.[59]

The conductivity of numerous alloys and other metallurgical products in the molten state, has been determined. The conductivity of iron sulphide is much superior to that of cuprous sulphide. Results with alloys of copper with tin, cadmium, and zinc demonstrate the existence of definite compounds having the composition, Cu_3Sn,Cu_2Cd_3,Cu_2Zn_3.[60] According to C. G. Fink,[61] the conductivity of a substance depends upon the shape and distribution of the component grains or particles and upon the presence or absence of thin films of secondary material on the particles. On this basis, the difference between two samples of the same batch of copper is due to one having the impurities uniformly dissolved throughout, while in the sample with lower conductivity the impurity forms a film around the particles of pure metal.

The conductivity of pure water is probably due to the carbon dioxide dissolved in it under the partial pressure of carbon dioxide in air, since the values calculated from the ionisation constant of carbonic acid, the mobility of HCO'_3, the carbon dioxide content of air, and the solubility of this gas in water, agree with direct determinations of conductivity.[62]

The conductivity of certain electrolytes in organic solvents has been determined, and the substances classified as strong or weak electrolytes, according to the rate at which their conductivities increase on dilution. In quinoline, which has a higher dielectric value than aniline, the salts used showed a higher conductivity, and therefore this property is certainly related to the conductivity of the dissolved substance.[63]

RESISTANCE.

Alloys continue to be devised for making resistance material. One such is composed of iron 75 to 25 % and of a metal having the properties of nickel or cobalt. One hundred parts of this alloy is combined with 10–30 parts of a metal of the chromium group.[64] According to another patent the resistor is composed of copper with 5 % manganese and 5 % of tin.[65] Nickel-chrome wire can be encased in a tube of the same alloy and insulated from it by a coating of aluminium silicate. Such a resistor is flexible and very convenient to handle.[66] Another resistor is made of a carbon base which is coated with a mixture of water-glass, clay, and graphite; the whole is then heated to fuse the coating to the base.[67] A tungsten resistance is made by embedding the metal between layers of silica, a current is then passed through the mass till the silica is fused.[68]

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[59] R Richter, *Z. Elektrochem*, 1916, **22**, 294, *J.*, 1916, 970

[60] *Z angew. Chem*, 1914, **27**, Ref, 707, *J*. 1915, 362.

[61] *Met. & Chem. Eng.*, 1916, **15**, 464; *J*, 1916, 1162.

[62] J Kendall, *J. Amer. Chem. Soc*, 1916, **38**, 1480; *J*, 1916, 926

[63] *J. Phys Chem*, 1915, **19**, 14; *J*, 1915, 175

Two types of resistometer suitable for measuring the resistance of molten material are described in a paper by R. G. Sherwood.[69] Alternating current is used because it is found that parasitic currents and electromotive forces become large and erratic above 500° C. A specially designed A.C. galvanometer is used and the resistance-temperature curves given for metals and alloys possess a linear character.

INSULATING MATERIALS

Much activity continues in this class of work. The mixtures produced generally include resinous or tarry materials, either alone, or mixed with mineral substances like silica, alumina, or asbestos.

Of those composed entirely of mineral substance, one consists of fused compounds of silicon, boron, and fluorine,[70] another is made by fusing a mixture of silica, boric anhydride, alumina, lithia, and an alkali;[71] the coefficient of expansion is very small, 0·00000056.

The insulating properties of asbestos may be greatly improved by removing all iron compounds by treatment with oxalic acid or other means, after which the resistance is found to be about one thousand times as great as that of the crude material.[72] Aluminium wire may be coated with an excellent non-conducting film of alumina, by making the wire the anode in a solution of sodium silicate. The film is flexible and will stand a pressure of 500 volts without short-circuiting to a similar wire next it.[73]

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[64] U.S. Pat. 1211943 (1917); *J.*, 1917, 295.
[65] U.S. Pat. 1217578 (1917); *J.*, 1917, 462.
[66] U.S. Pat. 1200352 (1916); *J.*, 1916, 1224.
[67] U.S. Pat. 1232843 (1917); *J.*, 1917, 1017.
[68] U.S. Pat. 1234973 (1917); *J.*, 1917, 1017.
[69] *J. Franklin Inst.*, 1916, **182**, 477; *J.*, 1916, 1162.
[70] U.S. Pat. 1226088 (1917); *J.*, 1917, 722.
[71] U.S. Pat. 1233486 (1917); *J.*, 1917, 1009.
[72] T. Schopper, *Gummi-Zeit.*, 1915, **29**, 1197; **30**, 243; *J.*, 1916, 931.
[73] *Trans. Amer. Elect. Soc.*, 1914, **26**, 137; *J.*, 1915, 360.

Several new insulators contain only organic materials. A condensation product of phenol with formaldehyde, dissolved in nitrobenzene, possesses a high dielectric constant; the solution boils above 120°C. This is mixed with naphthalene, and a filler such as china clay can be added.[74] Another is prepared from walrus or whale oil by heating until a dense fluid is obtained.[75] A non-inflammable insulating liquid[76] is produced by mixing pentachloroethane 93 %, dichloroethane 5 %, and hexachloroethane 2 %. Another insulator consists of a condensation product of phenols with anhydroformaldehyde-aniline, which is transformed into an infusible body by heating and then dissolved in a hydrocarbon of high insulating properties.[77]

An insulator which is flexible, non-inflammable, and cohesive is formed by oxidising a wax-like chlorinated naphthalene with concentrated nitric acid.[78] Chlorinated naphthalene figures in another insulator[79] which is made by distilling the chloronaphthalene mixed with a basic oxide in order to break up unstable addition products.

In another mixture,[80] shellac and resin are mixed with creosote oil, and while hot, alum is mixed into it; by this means a substance can be obtained which is easily melted, non-inflammable at its melting point, and flows well, but ultimately sets hard without appreciable shrinkage. According to a later patent, a filling material is added, also alum to render the mixture non-inflammable, magnesium carbonate to lighten it, and hydrated lime to make it set more readily. This substance is suitable for both heat and electrical insulation.

CORROSION AND PASSIVITY.

This important subject has received much attention during recent years and numerous explanations of the phenomena observed have been forthcoming.

The electrochemical explanation of corrosion and passivity of metals is now very largely accepted. A far-embracing discussion of the whole matter is recorded in the Faraday Society transactions[81] An important comparison of the corrosion of steels with their electrical properties has shown that a metal will dissolve in acid if the sum of its single potential and its overvoltage is less than the single potential of a hydrogen electrode. Overvoltage is here defined as the potential required to overcome the resistance offered by all metal surfaces to the liberation of gas. Using different specimens a determination was made of the single potential difference in dilute acids, of the overvoltage by the back E.M.F. method, and of the rate of corrosion of the specimens by acid and also when exposed to air.[82] Corrodibility as determined by the sum of the single potential and the overvoltage gave results parallel with those obtained by measuring the rate of solution of the metal in acid. The electrical method therefore appears well suited for determinations of corrodibility.

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[74] U S. Pat 1156452 (1915); *J.*, 1916 185

[75] U S Pat. 1170000 (1916); *J*, 1916, 550

[76] U S Pat 1235339 (1917); *J.*, 1917, 1053.

[77] Bakelite Co., U S. Pats 1216265, 1216266 (1917); *J*, 1917, 461

[78] U S. Pat. 1183423 (1916); *J*, 1916, 745.

[79] U.S. Pat 1196505 (1916); *J*, 1916, 1069.

[80] U.S. Pats. 1190814, 1190815 (1916), *J*, 1916, 897.

[81] *Trans. Farad. Soc*, 1914, **9**, 203, *see J*, 1913, 1113, 1114

The electrolytic behaviour of tungsten has been studied[83] and the single potential of the metal determined in $N/1$ solutions of acids, alkalis, and salts. It was found to be lowest with alkalis and highest in neutral salts, and it was ascertained that tungsten dissolves anodically and becomes passive in these solutions by the formation of a film of hydrated tungstic oxides.

An interesting investigation of polarisation and electrode processes with zinc, cadmium, copper, and nickel is connected with this subject.[84] Foerster,[85] in a paper on passivity, applies the term to all cases of abnormal resistance to the passage of ions into or out of a liquid, and in particular he discusses the discharge of halogens on platinum, the cathodic deposition of metals of the iron group, and the polarisation of the electrodes which retards the liberation of the ions.

DECOMPOSITION VOLTAGE. OVERVOLTAGE.

The decomposition potentials of alkali hydroxides and halides have been re-determined by Neumann and Bergve,[86] who question the accuracy of values accepted hitherto. Their values for fused caustic soda between 340° and 540° C. are 2·2–1·6 volts and the average temperature coefficient is $2{\cdot}95 \times 10^{-3}$. Fused alkali halides gave the following results: LiCl 2·62, NaCl 2·6, KCl 2·8, $CaCl_2$ 2·85 volts.

The subject of overvoltage has received considerable attention recently. In one paper[87] it is suggested that at the electrodes atomic forms of the elements are produced as unstable, reactive intermediates.

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[82] R. Hadfield and E. Newbery, *Proc. Roy. Soc.*, 1917, **A 93**, 56; *J.*, 1917, 219.

[83] *Met. & Chem. Eng.*, 1917, **16**, 40; *J.*, 1917, 221.

[84] *J.*, 1916, 51.

[85] F. Foerster, *Z. angew. Chem.*, 1915, **28**, 622; *J.*, 1916, 125.

[86] *Z. Elektrochem.*, 1915, **21**, 143; *J.*, 1915, 1088.

[87] C. W. Bennett and J. G. Thompson, *J. Phys. Chem.*, 1916, **20**, 296; *J.*, 1916, 607.

The change, molecule→atom→ion, is not completely reversible; the overvoltage is a measure of irreversibility and represents the excess of energy required to form a substance over that given by the re-solution of the substance. This definition applies to both gas and metal overvoltages. Haber's theory of a gas layer on the electrode seems improbable and does not fit the case of metals, but Nernst and Tafel suppose that ions must be driven into the electrode before liberation, and according to their view overvoltage represents the energy required to "drive in."

A great number of overvoltages have been determined by E. Newbery[88] and his investigations should prove very useful in technical work. He defines overvoltage as excess of back E.M F. over that of an oxygen or hydrogen electrode in the same electrolyte. The author points out that anodic overvoltages are considerably higher than cathodic ones and this renders the graded oxidation of organic and other compounds difficult. Cathodic overvoltage seems to be a periodic property of the elements. It is considered that overvoltage and passivity are in some way connected with the formation of compounds of the electrode material and the discharged ions. The original papers or abstracts should be consulted for detailed information.

Voltameters.

A silver voltameter has been described which is reported to be accurate to within a few hundredths per cent.[89]

According to T. W. Richards a correction is necessary on account of the electrolyte which becomes occluded in the silver deposits and which amounts to 0·001 to 0·025% .[90]

The "volume effect," that is, increase in weight of silver deposit in large voltameters over that observed in smaller ones, has been proved to be due to impurities in the electrolyte.[91]

Electrical Separation of Substances.

Under the influence of a considerable potential difference it is possible to separate finely divided particles from each other, or from gases and liquids, the constituents of emulsions may be separated and even a mixture of gases. In separating finely divided particles by means of a convective discharge, use is made of the different dielectric values of the particles themselves.[92] In the purification of suspended matter from gases, the gas is generally passed through a charged tube which contains an axial wire also charged. Oscillatory discharges of high frequency are employed.[93] In one form water or other liquid conductor runs down the discharge wire in order to prevent suspended matter from depositing upon it and so reducing its efficiency.[94]

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[88] *Trans Chem Soc*, 1916, **109**, 1051; 1066, 1359 , *J*, 1916, 1265 , 1917, 145.

[89] *Bull Bureau of Standards, U S A*, 1914, **10**, 475 , *J*, 1915, 91.

[90] *J. Amer Chem. Soc.*, 1915, **37**, 7 ; *J.*, 1915, 143

[91] *Bull Bureau of Standards, U S.A*, 1916, **13**, 447 ; *J*, 1917, 391.

[92] U.S. Pat. 1116951 (1914) ; *J.*, 1915, 37.

The method has been applied to clearing sulphuric acid mist, lead and zinc dust, as well as smoke from flue gases, using a direct current of 20,000 to 75,000 volts.[95] It has also been used for separating gases by cooling to produce a cloud and then using the discharge to precipitate the cloud.[96]

In a paper by W. W. Strong, attention is drawn to the fact that practice in this sphere is much in advance of theory owing to the rapid advance in the construction of suitable apparatus.

An outline of the underlying general principles is given and important matters which must be studied for future development are indicated.[97]

The coagulation of small particles by electrolysis has been applied in Landreth's process for purifying sewage.[98] Petroleum emulsion can be separated by subjecting it to the influence of an alternating current; the water coalesces as it passes through the "treater" and falls to the bottom.[99]

Separation of gases by direct-current discharge is in the experimental stage. F. Skaupy[100] has shown that when mercury and the inert gases are mixed with active gases, the latter pass to the cathode. Components of dissociable gases, such as aluminium chloride, can be completely separated and either deposited, or led off from the neighbourhood of the electrodes. Further, hydrocarbon gases undergo condensation with considerable reaction velocity, without carbonisation.

ATOMIC WEIGHTS.

The atomic weights of cadmium and zinc have been determined by electrolysis of solutions of the purified bromides, using a mercury cathode.[101]

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[93] U.S. Pat 1120561 (1914); *J.*, 1915, 91. Eng. Pat. 18357 (1913), *J.*, 1915, 804.

[94] Ger Pat 286912 (1913); *J.*, 1916, 243.

[95] *Eng. & Mining J.*, 1916, 101, 385; *J.*, 1916, 410.

[96] U.S. Pat 1204906 (1916); *J.*, 1917, 308.

[97] *Trans. Amer. Elect Soc.*, May, 1917; *J.*, 1917, 1137.

[98] U.S. Pat. 1131067 (1915); *J.*, 1915, 433.

[99] U.S. Pat. 1142759, 1142760 (1915); *J.*, 1915, 788.

[100] *Ber. Deuts. Phys. Ges.*, 1916, 18, 230; *J.*, 1916, 1068. *Ber.*, 1916, **49**, 2006; *J.*, 1916, 1162.

[101] G. P. Baxter, *J. Amer. Chem. Soc.*, 1916, **38**, 857; *J.*, 1916, 605.

REFINING OF METALS.

Copper refining forms the subject of several papers recently published The higher cost of labour in the series system of refining is equalled by the higher power cost of the multiple system, but the former must be provided with high-grade anode material, whereas lower-grade anodes and material running high in silver and copper may be used in the multiple system. On the whole, this system is replacing the older series system.[102] The crystalline structure of electro-deposited copper is the subject of several investigations.[103] Solution stratification can be used in the purification of electrolytes in copper refining.[104] Current losses in the multiple system are summarised by L. Addicks.[105] They include (*a*) current leakage to ground; (*b*) reactions involving deposition of impurities; (*c*) cathode shrinkage, due to re-solution of the copper by sulphuric acid or ferric salts. While 92% efficiency may be obtained by good working conditions, disregard of these may cause it to fall to 60%. The same author gives an interesting account of the impurities generally met with.[106] Silver, gold, tellurium, and selenium show a recovery of 97% while nickel passes into solution to the extent of 99%. Almost the whole of the arsenic passes into solution, together with iron and zinc, while lead, antimony, bismuth, and sulphur pass into the slimes. Foul electrolyte, after having most of its copper removed, is boiled down to remove nickel salts and then cooled to crystallise sodium salts. In another paper the same author describes the working up of the slimes.[107] Other particulars of this industry are given by F. Johnson.[108]

Tin refining from tinplate scrap is the subject of two patents,[109] and the deposition of the metal from various solutions, with a view to refining, has been tried.[110] The use of fluosilicic acid has been patented.[111]

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[102] P. L. Gill, *Eng. and Mining J.*, 1916, **101**, 9; *J.*, 1916, 181.

[103] Von Schwarz, *Int. Zeits. Metallog.*, 1915, **7**, 124; *J.*, 1916, 267. A. Sieverts and W. Wippelmann, *Z. anorg. Chem.*, 1915, **91**, 1; *J.*, 1916, 604.

[104] *J. Amer. Chem. Soc.*, 1915, **28**, 111; *J.*, 1915, 1096. Eng. Pat. 100318 (1916), *J.*, 1916, 1222.

[105] *Met. and Chem. Eng.*, 1917, **16**, 23; *J.*, 1917, 220. *Met. and Chem. Eng.*, 1916, **15**, 566; *J.*, 1916, 1263.

[106] *Met. and Chem. Eng.*, 1917, **16**, 687; *J.*, 1917, 966; *Met. and Chem. Eng.*, 1917, **17**, 169; *J.*, 1917, 1051

[107] *Amer. Inst. of Metals*, 1914, **8**, 165.

[108] *J.*, 1917, 803.

[109] **Fr. Pats.** 435936 (1911); 471078 (1915); *J.*, 1915, 182.

[110] *Trans. Amer. Electrochem. Soc.*, 1914, **26**, 133, *J.*, 1915, 360.

[111] **Eng. Pat.** 11818 (1915); *J.*, 1916, 364.

Antimony free from arsenic has not yet, apparently, been produced by electrolysis, although many methods have been tried.[112]

Gold bullion refining is now largely carried out in America by the improved Wohlwill process, using pulsating current. This process is compared with the older sulphuric acid and chlorine processes in a paper by T. K. Rose.[113] The electro-deposition of gold, silver, and copper from cyanide solutions, as practised on the Rand and in America, is discussed in a paper by G. H. Clevenger.[114]

EXTRACTION OF METALS.

The development of electrolytic and electro-metallurgical methods for producing metals has progressed rapidly since the outbreak of the war. Great progress is reported from America, where, in addition to electric furnace products such as steel and ferro-alloys, very large quantities of aluminium, zinc and magnesium have been produced. During 1916, the Anaconda Copper Co. was turning out electrolytic zinc at the rate of 100 tons per day, and this method of producing zinc has forced its way forward, while electric smelting of zinc ores has shown little progress.

Copper is now obtained in considerable quantities by electrolysis of the liquors obtained by leaching the ore with sulphuric acid[115] or ferric sulphate solution; the anode liquor during electrolysis becomes enriched in acid and is used repeatedly for leaching. A discussion of this industry took place recently in America.[116] Ferruginous ores are generally roasted before leaching, to convert the iron compounds to Fe_2O_3; after extraction, basic ferric sulphate may be precipitated by the addition of freshly oxidised ore.[117] In another process, a stream of sulphur dioxide is admitted in the anode region to prevent its polarization by oxygen.[118] The original process of Siemens und Halske has been modified by extracting the roasted ore with ferric sulphate in two steps, (1) using a cold dilute solution, (2) using a more concentrated and hot solution; most of the copper is leached out during the second extraction.[119]

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[112] A. G. Betts, *Trans. Amer. Elect. Soc.*, Sept., 1915; *J.*, 1915, 1097.

[113] *Trans. Inst. of Mining and Met.*, 1915, **24**, 35; *J.*, 1915, 495.

[114] *Trans. Amer. Elect. Soc.*, 1915, **28**, 263; *J.*, 1915, 1095.

[115] U.S. Pat. 1179522 (1916); *J.*, 1916, 640. U.S. Pat. 1232080 (1917); *J.*, 1917, 929.

[116] *Amer. Electrochem. Soc.*, April, 1915; *J.*, 1915, 619.

[117] U.S. Pat. 1134767 (1915); *J.*, 1915, 558.

[118] Eng. Pat. 108688 (1916); *J.*, 1917, 1100.

[119] U.S. Pat. 1136424 (1915).

Copper, gold, and silver ores can be extracted by electrolytic chlorine. A layer of mercury separates the anode from the cathode compartment and absorbs the sodium liberated; the extract then passes to the cathode, where the metal (Cu, Ag, Au) is deposited and the chlorine combines with the sodium amalgam to re-form sodium chloride, which is thus employed repeatedly.[120]

In a process patented by L. Addicks,[121] carbon anodes are used; these are depolarized by ferrous sulphate, and aluminium sulphate is added in sufficient quantity to counteract the solvent action of ferrous sulphate on the cathode copper. The author has given a full account of the research work which led to this process.[122] Zinc and lead are now extracted by electrolysis[123] after the ores have been leached with suitable solvents. Roasted zinc ores have been leached with calcium chloride liquors, in the presence of carbon dioxide, for some time past both in England and in Germany. In America, sulphuric acid leaching has developed during the last three years, the solution obtained being electrolysed with cathodes of copper or aluminium and anodes of lead or manganese dioxide. The Anaconda Copper Co. has completed a plant for producing 25 tons of metal a day by this method. At Bully Hill Mine in California the sulphate liquor is first precipitated with lime, and the resulting zinc hydroxide and calcium sulphate are suspended in the electrolyte to neutralise the acid as fast as it is liberated at the anode. The presence of a colloid in the liquor does not improve the deposit of zinc obtained.[124]

Lead is obtained by chloridising or sulphatising roasting, followed by leaching with saturated brine. On electrolysis a spongy metal is obtained, but this can be melted down if mixed with a reducing agent.

In connection with the winning of aluminium, a re-determination of the densities and melting points of various mixtures of cryolite, alumina, and fluorspar has been carried out by P. Pascal[125] and a process has been devised for recovering this metal from oil-refining residues by roasting part of the aluminium chloride and coke, mixing this with a fresh residue, and electrolysing the fused mass.[126]

Sodium production is the subject of a report by T. H. Norton,[127] who advocates the organisation of this industry and the utilization of both the Castner and the Darling processes. A cell has been devised on the Castner principle for producing sodium under a pressure of at least one pound per sq. in. The pressure raises the boiling point of the metal, and the loss by vaporisation is diminished.[128] Another improvement[129] in the electrolysis of alkali hydroxides in a fused state is the supplying continuously of fresh hydroxide to the cathode region, in order to prevent accumulation of water in the melt as a result of the reaction between the liberated hydroxyl ions. C. E. Acker[130] has patented the use of cyanides and cyanamides in the Ashcroft cell for producing sodium from fused chloride. He states that these compounds are more satisfactory than the chlorides.

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[120] U.S. Pat. 1137874 (1915); *J.*, 1915, 665.

[121] U.S. Pat. 1138921 (1915); *J.*, 1915, 666.

[122] *Amer. Electrochem. Soc.*, Sept., 1915; *J.*, 1915, 1096.

[123] *Met. and Chem. Eng.*, 1916, **14**, 30; *J.*, 1916, 182.

[124] Eng. Pat. 16326 (1915); *J.*, 1917, 37. *Atti R. Accad. Lincei*, 1914, [v] **23**, ii, 503; *J.*, 1915, 1147.

[125] *Rev. Mét.*, 1914, **11**, 1069; *J.*, 1915, 359.

[126] U.S. Pat. 1206874 (1916); *J.*, 1917, 84.

[127] *U.S. Comm. Report*, 1915, 297; *J.*, 1916, 111.

Nickel production also continues to receive attention. The production of nickel or copper-nickel anodes suitable for electrolysis work, and the separation of these two metals is the subject of two patents.[131] A paper by R. Riedel is devoted to the deposition of this metal from nickel chloride solutions with a view to utilisation of the liquors obtained after the deposition of copper from ores containing nickel; acetic acid is recommended for preventing spongy deposit.[132]

Pure iron can be obtained by electrolysis of solutions of fluoride or silicofluoride of the metal.[133]

Antimony can be obtained from stibnite by solution in caustic soda or sodium sulphide, the electrolyte being circulated between iron electrodes. Metal of high purity can be obtained in this way.[134] A fluoride solution acidified with hydrogen fluoride has proved a good medium for depositing antimony; an organic substance is added to prevent the formation of a crystalline deposit.[135]

Tungsten can be obtained by the electrolysis of fused sodium tungstate,[136] also by electrolysis of a fused lower oxide or mixture of oxides of the metal.[137]

Magnesium is probably now produced from carnallite by a contact electrode method similar to that used for calcium. A cathode of iron coated with zinc is stated to overcome effectively the globule trouble, and by using several cathodes near together large masses of magnesium may be collected.[138]

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[128] Fr. Pat. 466205 (1913); U.S. Pat. 1197137 (1916); J., 1914, 600; 1916, 1068.

[129] Eng. Pat. 17763 (1914); J., 1915, 967.

[130] U.S. Pat. 1142220 (1915); J., 1915, 803.

[131] U.S. Pats. 1128314, 1128316; J., 1915, 364.

[132] *Z. Elektrochem.*, 1915, **21**, 5; J., 1915, 555.

[133] Eng. Pat. 1437 (1914); J., 1915, 142.

[134] *J. Amer. Inst. Metals*, 1917, **11**, 83; J., 1917, 1180.

[135] F. C. Mathers, *Amer. Electrochem. Soc.*, May 1917; J., 1917, 1099.

[136] U.S. Pat. 1196699 (1916); J., 1916, 1067.

[137] U.S. Pat. 1202534 (1916); J., 1916, 1264.

Cerium can be obtained, in compact form, by electrolysis of the fused anhydrous chloride in an iron crucible cathode,[139] and the ferro-cerium alloys (Misch-metal) are obtained by electrolysis of the fused anhydrous chlorides of cerium, lanthanum, etc.; the fluorides are not so satisfactory, as the alloy does not separate in so coherent a form.[140]

The *rare earth metals* can be fractionally deposited as hydroxides on the cathode by electrolysis of a mixture in aqueous solution.[141]

A number of new cells or electrolytic tanks has been devised for dealing with the electrolytic separation or recovery of metals generally. In one of these, a series of plates form the electrodes at the bottom of a tank devised for recovering metallic particles in suspension. The liberated hydrogen carries the particles to the top and the outflowing product is cyanided, after which the cyanide solution may be electrolysed.[142]

Metalliferous pulp is treated in another cell by running it over mercury cathodes on which it amalgamates.[143] In another, an anode bell dipped into the electrolyte serves to draw off the anode gases—chlorine, oxygen, ozone—which can be utilised for extracting fresh ore.[144] Several modern cells are fitted so that the diaphragms or anodes can be kept in motion during electrolysis to prevent the anode from becoming coated with non-adherent material.[145] A special connection of electrodes has been devised to reduce the number of tank connections by one half, thus reducing the current losses due to these contacts; this is specially applicable to refining where a number of tanks are in series.[146] If the ore to be extracted is in contact with the cathode it is reduced, frequently, to the metal by the cathodic hydrogen.[147] It has been pointed out by G. H. Clevenger that generally electrolytic deposition of metals from cyanide solutions is much less complete than chemical precipitation, and it is more economical to complete the deposition in zinc boxes.[148]

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[138] U.S. Pat. 1190122 (1916); *J.*, 1916, 896.

[139] *Met. and Chem. Eng.*, 1917, **17**, 213; *J.*, 1917, 1099.

[140] *J.*, 1917, 373.

[141] U.S. Pat. 1115513 (1914).

[142] U.S. Pat. 1205207 (1916); *J.*, 1917, 88.

[143] U.S. Pat. 1233363 (1917); *J.*, 1917, 1014.

[144] U.S. Pat. 1183188 (1916), *J.*, 1916, 745.

[145] U.S. Pat. 1187903 (1916); *J.*, 1916, 897. U.S. Pat. 1191300 (1916), *J.*, 1916, 931.

[146] U.S. Pat. 1206963 (1916); *J.*, 1917, 146.

[147] Fr. Pat. 469516 (1913), *J.*, 1915, 36.

[148] *Eng. and Mining J.*, 1916, **102**, 579; *J.*, 1916, 1114.

ALLOYS. ELECTROPLATING.

The electro-deposition of alloys has not occupied much attention recently. An investigation of the various conditions affecting the deposition of electrolytic brass, deals with the separation potentials of zinc and copper from complex cyanide solutions and the influence of various addition reagents to the electrolyte.[149] An investigation by Bruni and Amadori deals with the production of various nickel-iron and nickel cobalt alloys by electrolysis of solutions of the mixed salts.[150] In addition to the production of ferro-cerium pyrophoric alloys, to which reference has been made, alloys with like properties have been prepared by electrolysis of solutions containing ferrous sulphate, magnesium chloride, and glycerin. The alloys contain carbon compounds, metal, and oxides, and yield sparks when scratched with metals.[151]

Electroplating solutions have formed the subject of several recent investigations. A boiling solution containing ammonium or sodium phosphates is recommended for platinum,[152] and various cyanide solutions have been studied in connection with copper-plating.[153] Plating with silver cyanide sometimes gives a non-adherent deposit which is apparently due to foreign metals, in the plated object, dissolving in the bath.[154] Bronze can be deposited from alkali oxalate-cyanide solutions of copper and tin.[155] For the plating of tin and aluminium on iron and other surfaces, phosphoric acid in the bath gives good results.[156] A general method for preparing plating baths has been devised, in which a solution of the metal is first precipitated as hydroxide, and this is dissolved in a suitable solvent (cyanide, etc.) to which sodium salicylate and ammonia are added.[157] A report to the Canadian Department of Mines states that plating with cobalt is, in most respects, superior to nickel plating.[158]

ELECTROLYTIC PRODUCTION OF HYDROGEN AND OXYGEN.

The application of the oxy-hydrogen flame to welding, cutting, and heavy lead work has called forth the invention of many new cells for the production of these gases. Many of these belong to the filter-press type which was first devised by O. Schmidt in 1890.[159] Most of them are built in such a way as to remove all risk of variation in gas pressure in the compartments and so diminish the chance of dangerous gas mixtures being formed. In one of these the electrodes have been specially designed to allow the gases to pass from them quickly, and the diaphragm is rendered gas-tight by a special fitting round the outer edge of the frames.[160] Another arrangement which has found favour is that of a tank negative, from the lid of which is suspended a bell-shaped anode surrounded by an asbestos sack diaphragm.[161] One of these is built to stand considerable pressure, so that the gases may be collected in storage vessels as they are evolved,[162] and in another cell special arrangement is made to enable the positive electrode to be removed without disturbing the diaphragm.[163] An account of the hydrogen-oxygen plant at the works of the Tennessee Copper Company has been given by L. O. Curran, who compares the low cost with that incurred by purchasing outside supplies of the gases.[164]

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[149] *Z. Elektrochem.*, 1916, **22**, 286; *J.*, 1916, 967.

[150] *J.*, 1915, 430.

[151] Kremann and Lorber, *Monats. Chemie*, 1914, **35**, 1387; *J.*, 1915, 719.

[152] *Elektrochem. Zeits.*, 1914, **21**, 193; *J.*, 1915, 495.

[153] *Met. and Chem. Eng.*, 1915, **13**, 255; *J.*, 1915, 496.

[154] Frary and Porter, *Amer. Elect. Soc.*, 1915, **28**, 307; *J.*, 1915, 1096.

[155] *Zeit. Elektrochem.*, 1915, **21**, 374; *J.*, 1915, 1086.

[156] Eng. Pat. 11011 (1915); *J.*, 1916, 930.

[157] Eng. Pat. 9957 (1915); *J.*, 1916, 545.

[158] *J. Ind. and Eng. Chem.*, 1915, **7**, 379; *J.*, 1915, 619.

Sterilization of Liquids.

Many patents have recently been granted for the electrolytic sterilization of sewage and putrescent liquors. In some of these the solid matter is precipitated as far as possible by the addition of lime, and then the filtered liquor is made to pass between electrodes where it comes under the purifying influence of electrolytic oxygen and ozone.[165] Sometimes the liquors are subject to electrolytic action during filtration, by a current passing between the filter-plates.[166] Alternating current is sometimes used and the liquor is passed through a narrow electrolytic zone between electrodes, with a high current density.[167] Electrolytic coagulation is used in another process for precipitating solid matter.[168]

Sterilization of milk is the subject of an interesting paper by F. C.

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[159] U S Pat 1211687 (1917), *J*, 1917, 295; also U S. Pats 1212229, 1214934 (1917).

[160] U S Pat 1181549 (1916); *J*, 1916, 1023

[161] U S Pat 1172885, 1172887 (1916); *J*, 1916, 476 U S Pat 1117185 (1914); *J.*, 1915, 37

[162] U S Pat 1154009 (1915), *J*, 1915, 1258

[163] U S. Pat. 1208722 (1916); *J.*, 1917, 146.

[164] *J*, 1917, 122

[165] U S Pat 1139778, 1139970 (1915); *J.*, 1915, 680. Eng Pat. 18564 (1914); *J.*, 1915, 978 *Met and Chem Eng.*, 1915, **13**, 735; *J.*, 1915, 1222.

[166] U.S. Pat. 1182316 (1916); *J.*, 1916, 706.

[167] Eng. Pat. 9567 (1914); *J.*, 1915, 631.

[168] U.S. Pat. 1146942 (1915); *J.*, 1915, 919.

Lewis, who describes apparatus for subjecting the milk to a high voltage current as it traverses a glass tube fitted with copper electrodes. The cost is small, harmful bacteria are exterminated, while taste, butter-forming and other necessary qualities are not impaired.

OZONE.

Many patents continue to be granted for apparatus for producing ozone. Most of these relate to improvements of the standard form consisting of electrodes between which sheets of dielectric are fixed.[169] Mica sheets are used in one machine, fitted in a frame of non-conducting material, and metallic gauze electrodes are fixed in the centre of each compartment.[170] In another device, two concentric glass tubes are used and mercury electrodes press against the glass, which has been etched or sand-blasted in order to give numerous fine points for discharge.[171]

Another ozoniser consists of a number of glass tubes which contain metallic threads, and around the outside a metallic spiral is wound.[172] A device has been patented for producing pure ozone by condensing it to liquid form, the more volatile nitrogen and oxygen being allowed to escape.[173] G. Lechner[174] gives an account of experiments with alternating current and interrupted continuous current, showing that the quantity of ozone produced is proportional to the quantity of electricity flowing through the reaction chamber. Sachs[175] points out that an ozoniser acts as a condenser, and above a certain limiting value of potential difference, discharge takes place. The ratio, quantity of electricity to maintain continual discharge/difference of potential between electrodes, gives a measure of the capacity of the ozoniser. Chemical changes in the gases facilitate the passage of discharge, because, with air, oxygen, and carbon dioxide, capacity increases with the rate at which the gas is passed through.

CAUSTIC SODA AND CHLORINE

Equal attention appears to have been given to the improvement of both the diaphragm cell and the bell cell, during the past three years. The mercury cell and the " fused salt " cell have seldom figured in the patent literature. Three new cells are built on the Hargreaves-Bird principle: one has a U-shaped permeable cathode which is placed i a container; steam is supplied to the cathode surface and forms alkal with the liberated metal.[176] The second is cylindrical and contains ring of carbon anodes in the brine compartment, which are surrounde by a diaphragm having a metal cathode cylinder, closely fitting roun its exterior surface, down which the alkali solution flows as it forms.[177] The third is a cell similar to the Hargreaves-Bird cell in constructio but having a reinforced concrete casing.[178] Three more cells are fitte with horizontal diaphragms. In one of these, by Siemens und Halsk A.-G., the diaphragm rests on a network of asbestos rope.[179] In another the brine enters by an opening slightly above the level of the diaphrag and flows across the cell; after leaving the cell, chlorine is expelle from the liquor by heating.[180] The third is similar to the Billiter-Siemen cell in construction.[181] Several improvements in the bell cell ar directed to improve the flow of liquor in this type.[182] In one cell of thi kind a diaphragm is fixed in the bell, dividing it into upper and lowe portions.[183] A report of "trial runs" with the Billiter-Leykam cel (which is a bell cell) is given by J. Yamasaki,[184] who records, alkal concentration 14–18%, current efficiency 92%, purity of chlorin 95%. A previous report on the high efficiency of this cell was give by Allmand.[185]

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[169] Eng Pat 107561, 108293 (1917); *J*, 1917, 969, 1016

[170] U S Pat 1218817 (1917)

[171] Knox Terpezone Co., U S. Pat 1130827 (1915), *J*, 1915, 433

[172] Fr. Pat. 473184 (1913); *J*., 1915, 509

[173] U.S. Pat. 1149254 (1915); *J*, 1915, 969

[174] *Z. Elektrochem.*, 1915, **21**, 309; *J*, 1915, 1101

[175] *Ann. Physik*, 1915, [IV], **47**, 886; *J*., 1915, 1257.

A mercury cell, patented by F. McDonald[186] contains a centra anode compartment enclosed by a perforated slate partition which i closely surrounded by asbestos and outside this is a mercury cathode In another cell,[187] the floor, on which the sodium amalgam flows fro anode to cathode compartment, has a series of ridges or impediment at right angles to the flow of mercury, which help to break up the surfac and keep it mobile.

A "fused salt" cell has been devised in which the collecting vessel for the alkali metal, is made of a zirconia mixture which resists the actio of both alkali and chlorine.[188]

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[176] U.S. Pat. 1149210, 1149211 (1915), *J.*, 1915, 969

[177] U.S. Pats. 1176540, 1176541 (1916); *J.*, 1916, 547

[178] U.S. Pat. 1125291 (1915); *J.*, 1916, 236.

[179] Ger. Pat. 286918 (1913); *J.*, 1916, 176

[180] Eng. Pat. 101440 (1916); *J.*, 1916, 1109

[181] U.S. Pat. 1138400 (1915)

[182] Eng. Pats. 101600 (1916), 25415 (1913), 22867 (1914); *J.*, 1917, 461; 1916, 55

[183] U.S. Pat. 1214775 (1917); *J.*, 1917, 391

[184] *J. Chem. Ind. Tokyo*, 1916, **19**, 257; *J.*, 1916, 598.

[185] *J.*, 1912, 1123. [186] U.S. Pat. 1117879 (1914); *J.*, 1915, 37.

[187] U.S. Pat. 1176551 (1916); *J.*, 1916, 601

[188] Ger. Pat. 291240 (1914); *J.*, 1916, 690.

The purification of electrolytic chlorine can be accomplished by passing the gas over a catalyst to accelerate the combination of the hydrogen with chlorine, and the resulting hydrogen chloride is then oxidised by passing over the same catalyst at a lower temperature.[189] Caustic soda can be purified by electrolysing the 50–60 % product (Na_2O) with a steel cathode at a temperature of 80°–175° C.; oxygen is liberated at the anode and metallic impurities are precipitated.[190]

The relation between evaporation plant for electrolytic soda and the source of power has been discussed; the evaporation plant which is best for water power will not prove the most economical if steam be the power source.[191]

HYPOCHLORITE, CHLORATE, PERCHLORATE.

According to one patent,[192] the gases produced by the electrolysis of chloride or alkaline sulphide liquors are first dried and then used for bleaching, disinfecting, or deodorizing.

Bleach liquor can be produced by electrolysing alkali chloride solutions with graphite anodes, relying upon a heavy current to cause the hydrogen to clear away quickly, before it has an opportunity of reducing the hypochlorite.[193] In another form of apparatus, deflectors on the anode cause the chlorine to be distributed throughout the liquid, and a similar mechanical contrivance ensures rapid removal of hydrogen.[194] A cell suitable for producing antiseptic solution from sea water has been fixed on board ship.[195]

Chlorates can be produced by electrolysing chloride solutions first at low temperature (35°), with graphite anodes, and then, in a second cell, at about 70° C., with platinum anodes and iron cathodes.[196] In a cell by A. G. Betts,[197] carbon anodes and magnesium cathodes are used with a coarse diaphragm to hinder the mixing of anode and cathode solutions; felspar is used as the raw material, and after roasting with lime the extracted liquor is used in the cell. A process by A. E. Gibbs for the production of both chlorate and perchlorate is the subject of another patent.[198]

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[189] U S Pat 1166521 (1916): *J*, 1916, 255

[190] U S Pat 1227453 (1917), *J*, 1917, 711

[191] *Trans Amer Elect Soc*, 1914, **26**, 215, *J*, 1915, 365

[192] Eng Pat 26726 (1913), *J*, 1915, 25.

[193] Eng. Pat 1672 (1915); *J*, 1915, 622.

[194] Eng. Pat 20714 (1914), *J*, 1915, 1139

[195] *Times*, Feb 1, 1916; *J*, 1916, 194

[196] U.S. Pat. 1143586 (1915); *J.*, 1915, 833.

[197] *Met. and Chem. Eng*, 1916, **15**, 627; *J*, 1917, 29

[198] U.S. Pat. 1173346 (1916); *J.*, 1916, 469.

VARIOUS INORGANIC PRODUCTS.

It is evident from the number of patents and papers, recently issued, which deal with the electrolytic production of inorganic substances, that the development of electro-chemistry in this particular province is being maintained. A brief reference to the various items will render possible a fairly complete view of recent progress. Alkali nitrates can be decomposed in a cell of the " bell " type; nitrites are formed at the cathode and the nitric acid produced at the anode is driven over by steam.[199] A paper by Crook and Booth shows the possibility of obtaining potassium cyanide and sulphate by electrolysing alkali thiocyanate solutions.[200]

In the production of potash by electrolysis of potassium sulphate solution, iron electrodes are used and the anodic mixture of $K_2SO_4 + Fe_2(SO_4)_3$ is suitable for a fertiliser.[201]

To obtain alkalis from kelp, this is electrolysed in a divided cell with a mercury cathode.[202]

Cuprous oxide, obtained by electrolysis of sodium chloride between copper electrodes, is improved in colour and uniformity by adding sodium nitrate to the bath and heating.[203]

The production of pure alumina from crude alkali aluminate is really an application of electro-osmosis, since the chemically precipitated alumina is finally subjected to current effect while encased in a diaphragm of viscose, to remove all alkali.[204]

Perborates can be obtained by electrolysing solutions of borax containing a considerable amount of sodium carbonate. The process is the subject of several patents and papers.[205]

Fractional electro-deposition of the rare earth hydroxides has already been mentioned and particulars of work on this subject will be found in two papers by L. M. Dennis and co-workers.[206]

Pure silicic acid, specially valuable for stabilizing colloids, can be prepared in a similar manner to alumina, already referred to, by enclosing alkali silicate in a diaphragmed anode compartment during electrolysis.[207]

[199] Eng. Pat. 16643 (1915); *J.*, 1917, 31

[200] *Met and Chem Eng*, 1916, **14**, 587; *J*, 1916, 688

[201] Fr Pat. 478371 (1914); *J.*, 1916, 1156

[202] U.S Pat. 1238600 (1917), *J*, 1917, 1127

[203] Eng. Pat. 14310 (1915), *J*, 1916, 1156

[204] Eng Pat. 6727 (1915); *J*, 1915, 904

[205] *Z Elektrochem.*, 1915, **21**, 253, *J.*, 1915, 1141 *Chem.-Zeit*, 1915, **39**, 806; *J*, 1916, 111. Eng. Pats. 14292 (1915), 100152, 100153, 100778, 102089, 102359, 106460 (1916); *J.*, 1916, 1261; 1917, 31, 83, 1047.

[206] *J. Amer. Chem. Soc.*, 1915, **37**, 131, 1963; *J*, 1915, 136, 1052.

[207] Fr. Pat. 471678 (1914); *J.*, 1915, 423.

Pure titanium dioxide is precipitated at the cathode during electrolysis of an acid solution containing this substance.[208]

Hydrazine and hydrazoic acid can be prepared by electrolytic oxidation of ammonia. The former is produced when aqueous ammonia is oxidized in the presence of sodium chloride and glue, and the hydrazine sulphate in presence of sulphuric acid can be further oxidized to hydrazoic acid.[209]

Arsenic acid and arsenates can be produced, in good yield, by electrolysis of arsenious oxide suspended in brine.[210]

Hydrosulphite production continues to be the subject of patents,[211] as well as the preparation of ammonium persulphate and from this of hydrogen peroxide.[212]

A good yield of concentrated sulphuric acid is obtained by electrolytic oxidation of sulphurous acid,[213] and in a similar manner selenic acid[214] is obtained from a nitric acid solution of SeO_2. Chromous salts are obtained in good yield by electrolytic reduction of violet and green chromic salts,[215] and an exhaustive study of the electrolytic oxidation of manganous salts has been made.[216] The electrolytic production of iodine is the subject of a paper, while the production of chlorine and bromine from potassium salt mother-liquors is dealt with in another. In the last paper the production simultaneously of a magnesium oxychloride cement is discussed.[217]

The production of cobalt oxides electrolytically has been patented; the process is also used for producing nickel oxides.[218]

PRODUCTION OF ORGANIC COMPOUNDS.

Recent literature records fair progress in the application of electrochemical methods to the production of organic compounds. Most of the papers and patents refer to reduction or oxidation processes; a few refer to synthetic methods.

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[208] Fr Pat 475642 (1914), *J*, 1916, 46 U S Pat 1235638 (1917), *J*, 1917, 1047

[209] *J. Amer Chem Soc*, 1915, **37**, 1114, *J*, 1915, 608

[210] U S Pat 1125086 (1915), *J*, 1915, 228

[211] Ger Pat 278588 (1912), *J*, 1915, 229

[212] Fr Pat 476816 (1914) Eng Pat 22711 (1914) U S Pat 1195560 (1916), *J*., 1915, 799; 1916, 634, 1059

[213] M de K Thompson, *Met and Chem Eng*, 1916, **15**, 677; *J*, 1917, 81.

[214] *Ber*, 1915, **48**, 1154, *J*, 1915, 904

[215] *Ber*, 1916, **49**, 1679; *J*, 1916, 1013

[216] *Z. Elektrochem*, 1915, **21**, 426, *J*, 1915, 1248

[217] *J*., 1916, 421; *Z angew Chem*, 1914, **27**, 569; *J*, 1915, 26

[218] U S Pat 1195211 (1916): *J*, 1916, 1059

Reduction by electrolysis has been applied in the following cases:—Di-secondary glycols by the reduction of saturated aliphatic aldehydes,[219] phenylhydroxylamine by reduction of nitrobenzene with zinc electrodes in neutral solution,[220] electrolytic hydrogenation of unsaturated fatty acids,[221] and the formation of ethylene from acetylene in the presence of chromous salts.[222] The formation of aminohydroxy-compounds is favoured by reducing nitro-compounds with a cathode composed of two or more metals.[223]

The reduction and oxidation of arsenical compounds has been investigated by Fichter and Elkind[224] and a general process has been patented for oxidizing or reducing organic substances when in an emulsified state.[225]

The electrolytic oxidation of cresols to the corresponding hydroxy-acids is the subject of another patent, and a process has been devised for electrolytic recovery of the mercury used in catalysing the conversion of acetylene to aldehyde.[226]

A study of the electrolytic chlorination products of benzene and toluene is described by Fichter and Glanzstein.[227]

An interesting synthesis of tartaric acid from carbon, steam, and chlorine has been devised, which follows the course, formate → oxalate → glyoxalic acid → tartaric acid.[228]

In two processes the silent discharge has been utilized for synthesising hydrocarbon gases, proceeding from higher to lower molecular weight or *vice versa.*[229]

Rubber can be coagulated by passing a current through the latex,[230] and a method has been devised for ageing wines and beers electrolytically.[231]

Electric Furnaces and Electric Furnace Products.

Very great activity has been displayed in the development of electric furnaces. Many of the improvements relate to furnaces built for special products, notably zinc or tin, and for gaseous reactions including the fixation of atmospheric nitrogen. Most of the patents refer to improvements in furnaces used for general heating and smelting purposes of the arc, resistor, or induction type.

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[219] Ger Pat 277392 (1913), Bayer und Co

[220] *Amer Elect Soc*, 1915, **28**, 345; *J*, 1915, 1083

[221] *Zeits. Elektrochem*, 1915, **21**, 444; *J*, 1915, 1271

[222] Ger. Pat 287565 (1913); *J.*, 1916, 142

[223] Eng. Pat. 18081 (1915); *J.*, 1917, 129.

[224] *Ber.*, 1916, **49**, 239; *J*, 1916, 383.

[225] Eng. Pat 15750 (1915); *J.*, 1916, 384.

[226] Eng. Pat 103709 (1916); *J*, 1917, 382. Eng Pat 10140 (1915); *J.*, 1916, 328.

[227] *Ber.*, 1916, **49**, 2473; *J.*, 1917, 207.

[228] U.S Pat 1190845 (1916); *J*, 1916, 944.

[229] U S. Pats. 1229042 and 1229886 (1917); *J*, 1917, 862, 863.

[230] *J.*, 1915, 1105.

[231] Fr Pat. 459141 (1912); *J.*, 1913, 1167.

Broadly speaking, the recent improvements are concerned with maintaining a constant current, controlling high temperatures,[232] the utilization of induction furnaces[233] and polyphase current,[234] and regulating apparatus for adjusting electrodes[235]

Auxiliary heating has been introduced, whereby the charge becomes heated by combustible gases before entering the furnace proper.[236]

Electrode material is the subject of several patents; in one of these steel turnings are incorporated with the carbon, while in another, hollow magnetite electrodes are used.[237] The furnace can be constructed so that parts are easily removed for renewal.[238]

Considerable attention has been given to providing furnaces with a suitable refractory lining in the make-up of which zirconia, magnesite, and carborundum figure.[239] Several patents relate to contrivances for keeping a molten charge in motion while in the furnace[240] Furnaces have been designed recently for working under increased pressure or under diminished pressure.[241]

An account of recent progress in the development of the electric furnace in non-ferrous metallurgy is given by D W. Miller,[242] and the same paper contains an outline of progress made recently at Sheffield in the production of ferro-alloys and special steels Another paper on the same subject, by A. Stansfield,[243] deals with electrolytic and electrothermal furnaces, and contains a concise account of the various products now made in the electric furnace. Two papers deal with the faults of electric furnaces and proposed methods of remedying these.[244]

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[232] *Bull. Bureau of Standards U S A*, 1914, 151, *J*, 1915, 91 *Proc Eng Soc W Pa*, 1915, **31**, 255, *J*, 1915, 661

[233] U S Pats. 1235629, 1235630 (1917), *J*, 1917, 1053 Eng Pat 370 (1914); *J*, 1915, 89

[234] Kilburn Scott, *J*, 1915, 113 U S Pat 1198625 (1916), *J*, 1916, 1116. Eng Pat 106626 (1916); *J*, 1917, 891

[235] U S Pat 1206603 (1916), *J*, 1917, 90

[236] U S. Pats 1177680 (1916), 1192050, 1208817 (1916), *J*, 1916, 641, 931; 1917, 224

[237] Eng. Pat. 106152 (1916) U S Pat 1226121 (1917), *J.*, 1917, 722.

[238] Eng Pat 107465 (1916); *J*, 1917, 969

[239] *Met and Chem Eng*, 1917, **17**, 415, *J*, 1917, 1236.

[240] Eng. Pat. 742 (1914); *J*, 1915, 877. Eng. Pat 17426 (1914); *J*, 1915, 912.

[241] Fr Pat. 480302 (1915), *Z. Elektrochem*, 1915, **21**, 54, *J*, 1915, 1152. *J*, *Wash. Acad. Sciences*, 1915, **5**, 277; *J.*, 1915, 621

[242] *Met. and Chem Eng*, 1917, **17**, 537

[243] *Inst. of Metals*, March, 1916; *J*, 1916, 473.

A large number of furnaces have been devised for the combined smelting of zinc ores and the distillation of the metal obtained. They are of arc or resistance type and frequently use polyphase current. Some of them are suitable for smelting tin and lead ores.

Furnaces suitable for bringing about reactions between gases have occupied much attention. They relate chiefly to the arc process for making nitric acid, but nitrogenous compounds generally are catered for. Furnaces for the production of aluminium nitride and abrasives are also well represented.

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[244] *Proc. Eng. Soc. W. Pa.*, 1915, **31**, 188; *Min. and Eng. World*, 1916, **44**, 955; *J.*, 1916, 845.

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OILS, FATS, AND WAXES

By E. R. Bolton, F.I.C., and Cecil Revis
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GENERAL.

Though the last year has not been marked by any phenomenal increase in our knowledge of the chemistry of oils, fats, and waxes, there is no doubt that the pressure of circumstances is having a beneficial effect on the industries connected with them, both in development of output and in a wider distribution and greater accuracy of knowledge of these very important economic substances. If only the impetus which has been given can be maintained when more normal circumstances shall remove the difficulties which now exist with regard to extension and erection of plant, there is no reason at all why Great Britain and her Colonies should not take the foremost place both in the production and manufacture of oils and fats, most certainly those of vegetable origin.

Much has been done by those in authority to secure to British manufacturers new sources of supply, and to encourage their use, so that the outlook is distinctly hopeful. The great scarcity of butter has resulted in the development of margarine manufacture, and the moment is at hand when the home production of this article should be able to exceed the demand. In this one direction alone there is great scope for ingenuity and discovery. It is to be hoped that the foolish ideas held with regard to margarine are rapidly filling a well-deserved grave, and any doubts regarding its digestibility and suitability as a valuable food product may now be regarded as laid to rest.

Owing to the necessity for restrictions, the figures for imports, &c., are not a reliable guide, but a few selected instances may help to show the general trend.

The imports of margarine have increased from 1,352,427 cwt. in 1912 to 2,752,866 cwt. in 1916. The imports of palm kernels alone have increased from 74,797 tons in 1914 to 241,501 tons in 1916, and the total import of nuts and kernels for the expression of oil has increased from 82,774 tons in 1912 to 373,022 tons in 1916. Satisfactory as these figures are, it must still be remembered that the import of palm kernels alone to Great Britain is less than to the port of Hamburg in 1914 (280,000 tons).

The palm kernel industry is distinctly a British one, and is being rightly fostered by those in authority, as copra cannot be fully controlled by us. Illustrating this are the figures of import of copra, which fell from 118,540 tons in 1915 to 62,400 in 1916, while palm kernels show the increase referred to above. The same applies to the restrictions for the import of refined oils which show a fall in the case of palm and palm kernel oils from 62,399 cwt. in 1914 to practically nothing in 1916. Refined cotton seed oil fell from 19,866 to 10,098 tons in the same period, while imports of oleo and refined tallow increased from 363,676 cwt. in 1914 to 650,584 cwt. in 1916. These figures taken together point to a great increase in the manufacture of edible oils in Great Britain.

A recent Bulletin of the Imperial Institute[1] gives an account of the development of the African palm oil industry, with some interesting conclusions as to the lines along which this industry should proceed, and there is no doubt that the next few years will see palm oil brought into this country as an edible fat.

That necessity is the mother of invention is well illustrated in a most instructive paper by Fahrion[2] on the sources of fat in Germany. The author shows that not only have existing sources been greatly extended, particularly in the case of sunflower (greatly neglected by other countries), but oil has been obtained in large quantities from the germs of all cereals, and even from coffee, while the saving of sewage fat has been enormous.

The falling off in the supply of edible oils has turned attention to the possibility of utilising fatty acids as a food material, and the subject has been investigated at the College of Agriculture, Edinburgh, by Lauder and Fagan.[3] The experimental animals seem to have done fairly well on a "feed" containing a certain proportion of the fatty acids obtained from coconut oil, but however satisfactory the results might be as an experiment, it is to be feared that unless the tendency of fatty acids to produce intense nausea can be overcome, there is little hope of increasing our supply of fatty foods for human consumption in this way.

An interesting paper on the influence of climatic conditions on vegetable oils has been published by Pigileveski.[4] According to this writer the iodine value of an oil among plants of the same sub-family increases as the distribution of the plant extends to the North, and he deduces from his results certain ideas as to the change in the composition of the glycerides present.

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[1] 1917, 15, 57; *J.*, 1917, 1017.

[2] *Z. angew. Chem.*, 1917, 30, 125; *J.*, 1917, 656.

[3] *J.*, 1917, 1069.

[4] *J. Russ. Phys. Chem. Soc.*, 1916, 48, 224; *J.*, 1917, 95.

The effect of storage on a large number of vegetable and animal oils has been examined by Gardner,[5] who finds that in general the saponification value increases while the iodine value decreases during such storage.

Incidentally reference may be made to attempts to utilise the residue from olive oil expression in the South of France, and as the ash of the residue contains nearly 50% of potash there certainly appears to be scope for its utilisation. According to Cruess and Christie,[6] 1000 tons of olive pomace are produced yearly in California, but they state that after extraction of the remaining oil, the residue has no value for manure or otherwise.

The bleaching of oils, fats, and waxes by a catalytic method in the presence of oxygen has been investigated by Hashmat Rai,[7] who shows that most metallic soaps have considerable bleaching effect, though varying in their power, and it is possible that the method may be employed in the bleaching of oils for soap work. Such a method will, of course, not replace the use of charcoal and fuller's earth in the edible oil industry. In this connection mention may be made of a method devised by Wickenden and Hassler[8] for comparing the efficiency of such charcoals by the use of a solution of Sudan III in kerosene. This test appears to differentiate between charcoals which are satisfactory for oils and those which are satisfactory for glycerin, and also demonstrates the superior efficiency of animal charcoals. The bleaching and absorptive capacity of fuller's earth from a valuation point of view, has been studied by Richert,[9] who has given a formula for arriving at the cost of bleaching with an unknown earth, compared with one of known absorptive power.

The polymerisation of tung oil, which has received so much attention lately, has perhaps rather led to the belief that the phenomenon is characteristic of that oil. Kronstein[10] maintains, however, that all fatty oils may undergo what he termed "mesomorphous polymerisation" on heating to a certain extent. He deduces practical applications from this theory and discusses the connection between drying capacity and polymerisation. His findings are, however, called in question by Fahrion,[11] who maintains that Kronstein's "distillation number" is no criterion of drying power, and is of the opinion that the polymerisation of tung oil is characteristic of that oil, as has been generally supposed.

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[5] *J. Ind. Eng. Chem.*, 1916, **8**, 997; *J.*, 1916, 1224.

[6] *J. Ind. Eng. Chem.*, 1917, **9**, 45; *J.*, 1917, 147.

[7] *J.*, 1917, 948.

[8] *J. Ind. Eng. Chem.*, 1916, **8**, 518; *J.*, 1916, 745.

[9] *J. Ind. Eng. Chem.*, 1917, **9**, 599; *J.*, 1917, 893.

[10] *Ber.*, 1916, **49**, 722; *J.*, 1916, 608.

It certainly seems doubtful that the gelatinous formations noted by Kronstein are the same as the jelly formed by tung oil, for otherwise it is credible that such observations would have been made before. Until Kronstein's work has been confirmed by other workers, Fahrion's objections should be regarded as carrying weight.

Special Oils and Fats.

The scarcity of oils and fats arising from the dislocation of the usual trade sources, has brought about a condition of affairs sufficiently acute to turn attention to many oleaginous products which hitherto have been of only scientific interest, or which have not been considered commercially available. Besides these products, many new sources of supply have been investigated, and the value of these supplies and their availability enquired into. As these products are naturally heterogeneous, it will be necessary to classify them roughly into groups in dealing with the work carried out in this connection.

Liquid Vegetable Oils.

Cotton seed oil A long and interesting paper on cotton seed products is given by Vakil,[13] in which varieties, exports, percentage yields, etc., are thoroughly dealt with, and some very interesting microscopical preparations of the seed are illustrated. The paper should be of interest to those dealing with cotton seed and the products thereof.

Sunflower, niger, and safflower seeds —The Bulletin of the Imperial Institute[14] deals with the cultivation and use of these seeds, drawing particular attention to the potash in the stems of the sunflower. Analyses of the oils are given. There is no doubt that for all these oils there is a great outlet for edible purposes, and more attention might well be given to the cultivation of these seeds, so that this bulletin is of special interest at the moment.

Spartium junceum.—Raffo,[15] in a paper dealing with a lipolytic enzyme present in the berries of this plant, records also considerable activity in this direction on sesamé, arachis, and cotton seed oils. Analysis of the oil shows it to be of the semi-drying class. Saponification value 198.6, iodine value 134, refractive index (Zeiss) at 25° C., 73.5.

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[11] *Ber.*, 1916, **49**, 1194; *J.*, 1916, 745

[13] *J.*, 1917, **36**, 685

[14] 1916, **14**, 88; *J.*, 1916, 696

[15] *Annali Chim. Appl.*, 1917, **7**, 157; *J.*, 1917, 657

Perilla oil.—Details of a sample of this oil, and also of the press cake, are published by Gardner.[16] He gives the following figures:—Specific gravity 0.937, refractive index 1.487, saponification value 193.4, and iodine value 193.3. Yield of oil 33.7 %. The sample was from Yokohama. Particulars as to the perilla seed crop in Japan are given in a U.S. Consular Report,[17] from which it appears that approximately 1,000,000 gallons of perilla oil were produced in the years 1912-13 respectively.

Palm fats. A very large number of palms are dealt with in extensive papers on Brazilian oil seeds by Bray and Elliot[18] and Bolton and Hewer.[19] These oil seeds will be of the greatest importance in the edible oil industry after the war.

Illipé nuts and Borneo tallow. The oils classified under this title are valuable but not very clearly defined, and a paper on these products will be found in the Bulletin of the Imperial Institute[20] which deals with the botanical species.

Stone and Pip Oils.

Cherry stone oil.—Rabak[21] refers to the quantities of cherry stones available, and states that something like 1,400 tons of stones are produced annually in the U.S. as a by-product. The kernels yield 30 % of oil by expression, whilst 8.5 % is obtained by extraction of the whole crushed stones. The oils are very similar and have a saponification value of approximately 180, iodine value of 93, and a Reichert-Meissl value of about 4. The chief difference is in the acetyl value, which is 3.4 for the stone oil and 12.7 for the kernel oil. The kernel press cake contains 1 % of volatile oil, giving 7.9 % of hydrocyanic acid and 68 % of benzoic acid.[22]

Orange pip oil. Orange pips are obtained in bulk as a by-product of marmalade manufacture, and analytical figures for the oil obtained from the pips have been given by Hewer.[23] These figures are very useful, as the data hitherto have been somewhat doubtful. Should it be possible to remove the bitter flavour, the oil should be available as an edible one.

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[16] *Oil, Paint and Drug Rep.*, 1917, **91**, 55; *J.*, 1917, 392.

[17] No. 105, 1917; *J.*, 1917, 723.

[18] *Analyst*, 1916, **41**, 298; *J.*, 1916, 1120.

[19] *Ibid.*, **42**, 35; *J.*, 1917, 345.

[20] 1915, **13**, 335; *J.*, 1915, 1213.

[21] *Bull. U.S. Dept. Agric.*, No. 350, 1916; *J.*, 1917, 159.

[22] *See infra*, Alpers, p. 310.

[23] *Analyst*, 1917, **42**, 271; *J.*, 1917, 969.

Other kernel oils.—The processes of obtaining oils from the kernels of cherries, plums, apricots, etc., are also dealt with by Alpers,[24] especially with regard to the difficulties due to cyanogenetic enzymes. By treating the mass of cracked stones with a solution of calcium or magnesium chloride of sp. gr. 1.5 the shells sink while the kernels are skimmed off. The insolubility of amygdalin in this solution largely minimises the effect of enzymes.

Canadian vine seeds.—Grape seed oil is of some interest at the moment, and the paper by Fachini and Dorta[25] is quite apropos. *Parthenocissus quinquefolia* yields an oil like olive oil, whilst *Ampelopsis quinquefolia* yields a butter like fat. The values do not differ markedly from those given by these authors for *Vitis vinifera*, and quoted by Lewkowitsch but the acetyl value is not given in the new investigation.

Drying Oils.

Para rubber seed oil.—An interesting paper is communicated by Uchida,[26] mentioning this oil among others. Several other oils are also dealt with, viz. *Shiromoji* seed, *Callophyllum*, *Hernandia* seed, *Hakumboku* seed, *Akebi* seed, *Kuromoji* seed, *Aburachan* seed, *Magnolia* pulp and seed, *tea* seed oils, and *lumbang* oil.

Gardner[27] gives analyses of the oil and cake of the kernels of *Aleurites moluccana*. The oil, though like tung oil, does not polymerise. It has purgative properties.

Brill and Agcaoili,[28] dealing with Philippine oil seeds, state that lumbang oil (*Aleurites moluccana*) can be distinguished from the product of *A. trisperma* by the insolubility of the former oil in alcohol.

Manketti nuts.—A sample of these South-West African nuts has been examined by the Imperial Institute Laboratory,[29] who allocate the oil to the semi-drying class. It is not considered by them to be of much value. Their figures differ somewhat from those of Sprinkmeyer and Diedrichs,[30] who consider the oil suitable for linoleum, and the cake valuable as a food-stuff.

[24] *Chem.-Zeit.*, 1916, **40**, 615; *J.*, 1916, 93..

[25] *Annali Chim. Appl.*, 1916, **5**, 301; *J.*, 1916, 931.

J., 1916, 1089.

Oil, Paint and Drug Rep., 1917, **91**, 55; *J.*, 1917, 392.

Philippine J. Sci., 1915, **10A**, 105; *J.*, 1916, 609.

Bull. Imp. Inst., 1917, **15**, 35; *J.*, 1917, 1018.

Z. Unters. Nahr. Genussm., 1914, **27**, 113; *J.*, 1914, 1097.

Tung oil —The effect of heat on Chinese wood oil at temperatures of 200°-300° C has been studied by Krumbhaar[31] The oil was heated in the presence of carbon dioxide, and the effect on the various constants of the oil noted. Considerable change in the iodine value took place, and, as would be expected, in viscosity. In the case of the iodine value, the oil which had an initial figure of 160·3 was reduced to a value of 134·5 after four hours' heating at 200° C The saponification value in this time fell from 193·2 to 190·1 Parallel experiments were carried out with linseed oil, and enormous increases in viscosity took place with this latter oil The author leans to the view that the difference between the polymerisation is only one of degree and not of kind[32]

The writers of this article have noticed a very perfect gelatinisation on heating, in the presence of carbon dioxide, the oil from the seeds of *Couepia grandiflora*, but in this case the setting appears to be accompanied by the setting free of gas bubbles in considerable quantity. The work on this oil will be published shortly

Browne[33] also gives some figures for Chinese wood oil, and details specification tests In this connection attention may be drawn to a U S Consular Report[34] on the use and output of Pawlownia oil, which is probably Japanese wood oil, but they state that the oil has not as yet any commercial significance It is rather unfortunate that this Report has apparently again introduced the confusion in Japanese wood oil which is derived from *Paulownia imperialis*, and not from *Aleurites cordata*, which this Report states as the source of Pawlownia oil.

FISH OILS

Several communications have been made by Tsujimoto[35] on the liver oils of various fishes These deal with the liver oils of sunfish, ray, seal, and shark In the last-named he finds a highly unsaturated hydrocarbon which on hydrogenation gives an oil resembling "liquid paraffin," and melting at 35 C. He terms this hydrocarbon "Squalene" It is quite possible that the substance is identical with the "Spinacene" of Chapman[36] This substance, obtained from the liver oil of certain of the shark family, has been fully investigated by this latter author, and various derivatives prepared from it. The figures given for the oil from the livers of sharks caught off the Moroccan coast are :-Sp. gr. 15°/15° C., 0·8666 ; saponification value, 22·5 ; iodine value (Wijs), 358 % ; unsaponifiable matter, 89·1 %, and iodine value of the latter, 376·2. The unsaponifiable matter distilled under reduced pressure was a colourless mobile oil, boiling at 280° C. under 17 mm. pressure. The formula is given as either $C_{27}H_{44}$ or $C_{28}H_{44}$. In a later paper[37] the same author draws attention to the need of revising the accepted constants for shark liver oil. He further states that the hydrocarbon can be distinguished from hydrocarbons that might be added as an adulterant by its high iodine value, and the yield of bromides insoluble in ether.

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[31] *Chem.-Zeit.*, 1916, **40**, 987 *J.*, 1916, 1224

[32] *See* Kronstein and Fahrion, *ante* pp 307, 308

[33] *Chem News*, 1916, **114**, 123, *J.*, 1916, 1023

[34] *U S Cons Rep* No 105, 1917, *J.*, 1917, 723

[35] *Kogyo Kwagaku Zasshi*, 1916, **19**, 715, 833, *J Ind Eng Chem*, 1916, **8**, 889, *J.*, 1916, 1069, 1121 and 1163

[36] *Chem Soc. Trans*, 1917, **111**, 56; *J.*, 1917, 392

Calamary oil. This oil, obtained from the liver and internal organs of cuttle fish, is described by Tsujimoto.[38] The oil has a high iodine value, 177 %, but the unsaponifiable matter was only 1·14 %. It is easily hydrogenated to a white fat resembling tallow, with an iodine value of 49 %.

ANALYTICAL PROCESSES.

Progress on the analytical side of the examination of oils and fats has not shown any marked features. So much time is necessarily allocated by those usually engaged in such work to industrial requirements, that the temporary suspension of investigation work has been inevitable. This is no doubt unfortunate, as in no section of food analysis is investigation so urgently needed. As was remarked in the section on "Special Oils and Fats," sources of supply from quite new seeds and nuts are multiplying, but beyond the usual determination of constants no identification of these new products would be possible in the vast majority of cases if they appeared in mixtures with other fats. Attempts are being made to determine the actual acids present in certain fats as glycerides, and the results are very interesting. Such work is, however, laborious and possibly open to question from the point of view of technique, but at the moment it appears to be a step in the right direction. It will only be when we are able to determine in a quantitative manner at least some of the acids present in a fatty mixture, that any certainty will enter into fat analysis. Chemists are much in the same position as they were with regard to proteins a few years back, and it is to be hoped that scientific research in the near future will show the same strides in the chemistry of fats as it has in that of proteins. On the surface, investigations into separation of acids do not appear hopeful, but if it lead to the identification of certain glycerides, the knowledge so acquired may assume more important aspects.

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[37] *Analyst*, 1917, **42**, 161 ; *J.*, 1917, 602.

[38] *J. Ind. Eng. Chem.*, 1916, **8**, 801 ; *J.*, 1916, 1024.

The chemistry of hardened fats is another field in which so far few tangible results have been produced.

In dealing with the progress of last year, it has only been possible to mention the papers published under an alphabetical category.

Arachidic acid.—Two new methods of detecting arachidic acid have been put forward, one by Kerr,[39] who separates the arachidic acid by precipitation with alcoholic magnesium acetate and recrystallises the fatty acids so obtained; the other by Brazzo and Vigdorcik,[40] who separate the saturated acids by lead acetate, afterwards liberating these acids and recrystallising. It is doubtful whether either method has any advantage over Bellier's process as modified by Evers, or the ordinary Renard method, and difficulties would certainly arise in presence of such acids as stearic and palmitic.

Benzoic acid.—Stadlin[41] proposes to detect this acid in fats by dialysis in alcoholic solution, afterwards evaporating and extracting the dialysate with ether.

Butter fat.—The presence of stearic acid has been again investigated by Holland, Reed, and Buckley,[42] using Hehner and Mitchell's method, and they find 7·22 present in the insoluble fatty acids. They point out some of the sources of error in that method, and show how they may be avoided to some extent. A separation of the glycerides of butter fat has also been carried out by Crowther and Hynd,[43] who prepare the esters and separate by fractional distillation. This paper is of considerable interest as illustrating a method of solving the difficult problem of separating the glycerides present in oils and fats. Mention may be made of work by Phelps and Palmer[44] on the separation of butyric acid in mixtures containing formic and acetic acids, by means of quinine, the method being based on the solubility of quinine butyrate in carbon tetrachloride and the insolubility of the other quinine salts.

The value of the *Reichert-Meissl-Polenske method* for the estimation of coconut and palm kernel oils in mixtures has been called in question by Elsdon.[45] This author attempts to show that the Shrewsbury and Knapp method is more satisfactory, but the figures given scarcely bear out this contention, though possibly the two methods may be made to afford mutual confirmation in doubtful cases.

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[39] *J. Ind. Eng. Chem.*, 1916, **8**, 904; *J.*, 1916, 1121.

[40] *Annali Chim. Appl.*, 1916, **6**, 179; *J.*, 1917, 90.

[41] *Chem.-Zeit.*, 1916, **40**, 770; *J.*, 1916, 1128.

[42] *J. Agric. Res.*, 1916, **6**, 101; *J.*, 1916, 649.

[43] *Biochem. J.*, 1917, **11**, 139; *J.*, 1917, 1059.

[44] *J. Biol. Chem.*, 1917, **29**, 199; *J.*, 1917, 567.

[45] *Analyst*, 1917, **42**, 295, 298; *J.*, 1917, 1103.

Colour tests.—The various colour tests for oils have been investigated by Gill,[46] who points out many of the reasons which lead to inconclusive results with these tests, and emphasises the fact that in many cases they are not to be too much relied upon.

Croton oil.—A test for the identification of this oil is put forward by Comte,[47] the author stating that an alcoholic solution of a mixture containing this oil, when poured on to a concentrated solution o sodium or potassium hydroxide and warmed in boiling water, gives an intense reddish-brown or violet ring at the junction of the liquids. This reaction is stated to be characteristic.

Glycerol.—A modification of the bichromate method for the estimation of glycerol is given by Little and Fenner.[48] This method would appear to be somewhat more rapid than the official method, and is stated to give excellent results. For the estimation of glycerol in fatty oils, Bull[49] again suggests the use of sodium glyceroxide, and the method as employed by him is stated to give results closely approximating to those obtained by calculation from the ester values.

Hydroxy fatty acids.—The possibility of not extracting these acids from mixtures when using ether or light petroleum spirit is drawn attention to by Hodes,[50] who prefers to use a boiling mixture of equa volumes of chloroform and alcohol (96/100 %) which obviates this danger.

Linseed oil.—A paper by Friend[51] on the effect of heat and oxidation may be noted at this point, as the results obtained are of some little interest, though the paper deals largely with the theory of the changes taking place during drying.

Maumené value.—An attempt has been made by Marden and Dover[52] to standardise this value by using a Dewar vacuum tube of known thermal capacity. The effect of alterations in the sulphuric acid is dealt with, and the values for a number of oils have been determined under the new conditions.

Marine animal oils.—Marcusson and von Huber[53] state that when marine animal oils have been heated out of contact with oxygen, they no longer give the octobromide test, but still yield a positive result to Tortelli and Jaffe's reaction.[54] They also give methods for distinguishing these oils from their hydrogenated products.

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[46] *J. Ind. Eng. Chem.*, 1917, **9**, 136; *J.*, 1917, 345.

[47] *J. Pharm. Chim.*, 1916, **14**, 38; *J.*, 1916, 898.

[48] *J. Amer. Leather Chem. Assoc.*, 1917, **12**, 254; *J.*, 1917, 893.

[49] *Chem.-Zeit.*, 1916, **40**, 690; *J.*, 1916, 1069.

[50] *Chem.-Zeit.*, 1917, **41**, 492.

[51] *Chem. Soc. Trans.*, 1917, **111**, 162; *J.*, 1917, 462.

[52] *J. Ind. Eng. Chem.*, 1917, **9**, 858; *J.*, 1917, 1138.

[53] *Mitt. K. Materialpruf.*, 1916, **34**, 56; *J.*, 1916, 1121.

Melting point.—A new method of determination is described by Monhaupt,[55] this being based on the temperature at which a pointed wire penetrates a capillary column of the solidified fat. This does not appear to offer any advantage over the ordinary methods employed, and only adds another somewhat dilettante procedure to a long list of others.

Palm kernel oil.—Salway[56] has examined the substances which pass over with the steam in the process of deodorising this oil, and finds that the mixture consists of free fatty acids and neutral fat, with about 1 of a volatile oil which on investigation appears to be methyl-nonyl ketone. Coconut oil, on the other hand, appeared to give methyl-heptyl ketone and methylundecyl ketone. It would be of considerable interest if the substances derived from other oils in a similar manner could be investigated.

Soya beans.—Brill[57] states that soya beans from China, America, and Japan contain a soluble substance in alcohol and ether which gives the ordinary salicylic acid reaction with ferric chloride, but does not react with Jorissen's reagent (potassium nitrite, acetic acid, and a trace of copper sulphate). This reaction is considered to be due to the presence of maltol produced by enzyme action.

Phytosterol acetate test.—The digitonin method for separating the sterols from oils and fats has been the subject of several papers, mostly of a polemical character. The controversy is still raging round the question of the necessity or otherwise of previous saponification. To those who are interested in this question and are able to obtain digitonin the papers mentioned[58] will be of interest.

Fatty acids.—A useful paper on the solubility of lithium and magnesium salts of lauric and myristic acids, in the presence of higher acids, is contributed by Jacobsen and Holmes.[59] These results are the outcome of a general study of the salts of these acids with lithium, magnesium, glucinum, barium, lead, and silver in a large number of solvents

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[54] *J.*, 1914, 1061; 1915, 1012.

[55] *Chem.-Zeit.*, 1916, **40**, 676; *J.*, 1916, 971.

[56] *Chem. Soc. Trans.*, 1917, **111**, 407; *J.*, 1917, 1184.

[57] *Philippine J. Science*, 1916, **11** A, 81; *J.*, 1916, 1077.

[58] Kuhn and Werwerinke (*Zeit. Unters. Nahr. Genussm.*, 1914, **28**, 369); Klostermann and Opitz (*ibid.* 138); Olig (*ibid.* 129); Pfeffer (*ibid.* 1916, **31**, 38); Wagner (*ibid.* 1915, **30**, 265); Kund, Bengen, and Werwerinke (*ibid.* 1915, **29**, 321); Prescher (*ibid.* 1917, **33**, 77).

[59] *J. Biol. Chem.*, 1916, **25**, 55; *J.*, 1916, 696.

De Conno[60] has applied the preparation of aromatic amines of the fatty acids to the analysis of fats. These amines are prepared by heating the glycerides with aniline in sealed tubes. The product is fractionated under reduced pressure and the fatty acids re-formed from the fractions. Many compounds of the fatty acids for the purpose of identification are detailed.

Relationship between constants. Backer[61] deduces a formula for the relationship between the refractive index, density, saponification and iodine values of oils and fats. This is worthy of remark, as too little attention has been given to this point in connection with analysis, and comparison of values is often of the greatest service. The formula given is:—

$$\frac{n_t^2 - 1}{n_t^2 + 2} \times \frac{100}{d_4^t} = 33.07 + 0.00075\,I + 0.01375\,V + 0.002\,(t - 15)$$

where n = refractive index, d = sp. gravity, V = saponification value, and I = iodine value.

Oil testing.—Gill[62] publishes certain tests for oils based on the salting out of their soaps, the test being made finally by titration with a standard solution of sodium chloride. Differences are noted between different oils, but the test does not appear to be of great value. The author also records a test for the quantity of gelatinised matters present in linseed oil.

RANCIDITY.

The question of rancidity in fats is always to the fore, and elucidation does not appear to be any nearer, in spite of the work that is published from time to time on the subject. It will be sufficient to note the few investigations which have been carried out, and to draw attention to the authors' conclusions from their work.

Rather[63] has examined a large quantity of cotton seed which had been kept piled in storage for 77 days. Much heating took place and a great increase in free fatty acids and total acidity was noted. He argues that this latter increase is entirely connected with the heating, and that time of storage is not a factor. It may be noted that hydrolysis may proceed to 70 % of the fat and 33 % of the protein present. In connection with these results it may be stated that the cause of rancidity in palm kernel cake has been attributed to a zymogen which, in the presence of warmth and moisture, produces a lipase and so brings about the formation of fatty acids. Heating of the meal to 70° C. practically prevented any change.

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[60] *Gaz. Chim. Ital.*, 1917, **47**, I., 93; *J.*, 1917, 511.

[61] *Chem. Weekblad*, 1916, **35**, 954; *J.*, 1916, 1163.

[62] *J. Ind. Eng. Chem.*, 1917, **9**, 136; *J.*, 1917, 345.

[63] *J. Ind. Eng. Chem.*, 1916, **8**, 604; *J.*, 1916, 898.

A method of testing for the presence of rancidity in fat is given by Vintilesco and Popesco.[64] This is based on the assumption that fats absorb oxygen from the air and form peroxides which are the cause of the rancid flavour. This being the case, the presence of such change is detected by shaking the fat with hæmoglobin, guaiacum tincture, and water, when, if such oxidation has taken place, the usual blue colour is produced. The authors expressly state that the reaction is not due to free fatty acids, and so seem to have in mind, what is so often forgotten, that free fatty acidity and rancidity are not the same thing.

A method of estimating the rancidity in fats has been devised by Issoglio[65] based on the number of milligrams of oxygen necessary to oxidise the steam distillate from 100 grams of the fat. This quantity he terms the "oxidisability number," and should be, when using the formula given by him, from 3 to 10 for normal fats, while those which are rancid give numbers from 15 upwards.

Though scarcely to be classified under the heading of rancidity, attention must be drawn to a very interesting investigation by Dyer[66] on progressive oxidation in cold storage butter. The falling off in flavour during cold storage is a matter of considerable moment, as the loss is accompanied by a depreciation in market value. The effect of storage has never been clearly understood, it only being known that sweet cream butter deteriorated less than sour cream butter. The general conclusions of the author are that the falling off in flavour is not due to action on the fat as usually assumed, but to chemical changes in the non-fatty constituents, and that this change is proportional to the acidity of the cream used in the preparation of the butter.

GLYCERIDES AND FATTY ACIDS

Reference was made above to the possible utility, in the future, of methods devised for the purpose of separating the glycerides in fats, and an attempt has been made in this direction by Seidenberg,[67] based on the use of two solvents, one of which is more volatile, and has a greater solvent action on the glycerides. Using this method, he has separated two mixed glycerides from tallow, and has further applied

[64] *J. Pharm. Chim.*, 1915, **12**, 318; *J.*, 1915, 1214.

[65] *Atti R. Accad. Sci. Torino*, 1916, **51**, 552; *J.*, 1916, 858.

[66] *J. Agric. Res.*, 1916, **6**, 927; *J.*, 1916, 1077.

[67] *J. Ind. Eng. Chem.*, 1917, **9**, 855; *J.*, 1917, 1138.

the results to the examination of butter. The chief drawback appears to be the expense of the method, but at present this is common to nearly all such methods.

The hydrolysis of fats by the lipase of *Ricinus communis* has been studied by Tancov,[68] using sulphuric acid as the activator, and the velocity of the reaction appears to depend upon the speed of decomposition of intermediate products formed by the enzyme with the acid products of hydrolysis.

The action of potassium hydroxide, when fused with hydroxy-fatty acids of high molecular weight, such as dihydroxy-stearic acid, has been investigated by Eckert.[69] The author infers from his results that during the reaction a direct shifting of the double linkage in the chain takes place. Mascarelli,[70] continuing his work published with Sanna[71] on erucic, brassidic, and isoerucic acids, has come to the conclusion by the use of cryoscopic and eutectic methods, that the two former acids are isomers, the relationship being similar to that of oleic and elaidic acids, while brassidic and isoerucic acid are not isomers. Erucic and isoerucic acids are probably the cis- and trans-forms of the same acid.

HARDENED OILS

The importance of hardened oils continues to increase, a fact for which there need be little surprise when the want which hardened oils supply in the edible oil industry, as well as that of soap and candles, is considered. There has always been a large demand for cheap solid fats for margarine, which even the ever-increasing output of coconut and palm kernel products seems unable to supply, and the ready conversion of liquid oils into harder fats has been of the greatest value. The future alone will show whether they will survive in the edible oil industry in face of the many and various new solid vegetable fats which seem likely to appear on the market, for in this, as in all cases, cheapness will rule the market. It is possibly easier to produce a tasteless and odourless fat when the refining process includes the hydrogenation methods than when simple deodorisation is employed, and this may be a factor in the scale.

The actual chemistry of the process, particularly with regard to the state of the catalyst, still appears to be giving rise to discussion. Normann[72] replies to attacks by Siegmund and Suida[73] and by Erdmann as to the presence of metallic nickel in the catalyst, and considers the idea of a nickel suboxide unreasonable. This is practically the view held by Meigen,[74] who records a number of experiments in which he demonstrated the presence of metallic nickel in the catalyst after action. Siegmund and Suida,[75] in their attempts to prove the necessity for the presence of their somewhat nebulous nickel suboxide, tried a number of mixtures such as basic nickel carbonate, nickel formate, nickel and nickelous oxide, and metallic nickel alone, as the catalysts, and they believe that their experiments show that nickel oxide acts as the carrier in the presence of water. It has been noted by Mannich and Thiele[76] that the addition of animal charcoal increases the absorptive capacity of palladium for hydrogen very considerably, and they prepare a catalyst by shaking animal charcoal with palladium chloride in hydrogen until gas ceases to be absorbed. The powder obtained, after drying, appears to keep well, and according to the authors, has very powerful hardening capacity, and they cite a number of liquid vegetable oils in which the iodine value has been easily reduced below 1 . This procedure may be considered somewhat in the light of a useful laboratory method.

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[68] *J Russ Phys Chem Soc*, 1916, **48**, 287; *J Chem Soc*, abs, 1917, **1**, 182

[69] *Monatsh Chem*, 1917, **38**, 1; *J*, 1917, 892.

[70] *Gazz Chim Ital*, 1917, **47**, I, 160

[71] *Ibid*, II, 335

[72] *Chem.-Zeit*, 1916, **40**, 381

[73] *J prakt Chem*, 1915, II, **91**, 442

The great bugbear of the hydrogenation process has always been the liability to deterioration on the part of the catalyst, owing to action of impurities in the hydrogen or the fat employed. This matter has been dealt with in the case of low grade oils, particularly fish and whale oils, by Ellis and Wells,[77] who show that in such cases something is taken up from the oil which rapidly causes the catalyst to become inactive. As, however, the poisonous effect appears to be rather of the nature of adsorption, it would seem that the injurious effect might be minimised by a preparatory treatment, and this the authors tried with success.

The changes in the amount, character, and chemical characteristics of the glycerides in oils during hydrogenation, and the effect on the various constants, have been investigated very carefully by Moore, Richter, and Van Arsdel,[78] using cotton seed oil for the purpose. The changes found have all been expressed graphically, and the conditions of hydrogenation and their effects very closely followed, and attention has also been given to the effect of catalyst poisons. The paper is one which should be carefully studied by those interested in hydrogenation.

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[74] *J. prakt. Chem.*, 1915, **92**, 390; *J.*, 1916, 262.

[75] *Loc. cit.*

[76] *Ber. Deuts. Pharm. Ges.*, 1916, **26**, 36; *J.*, 1916, 518.

[77] *J. Ind. Eng. Chem.*, 1916, **8**, 886; *J.*, 1916, 1121.

[78] *Ibid.*, 1917, **9**, 451; *J.*, 1917, 657.

Hardened whale oil has been investigated by Svendsen.[79] The hardening had been only partial, as the iodine value of the sample was 59·8, but it gave no insoluble bromides. The author separated quantitatively the fatty acids present, and among them found arachidic and behenic acids, which are probably the results of the process, and the quantity of Bull's C_{16} acid was only found to be 0·6 %.

On the tests for hydrogenated oils little is forthcoming, but a paper by Prescher[80] on the various colour reactions is of interest. Hardened marine animal oils, he states, are indicated by the colour reactions of Tortelli and Jaffe,[81] together with Kreis and Roth's test for arachidic acid, and the results are useful if taken in conjunction with a positive test for cholesterol, which rather appears to support Svendsen's results. Sesame oil may be detected by the Solstein test. Bellier's reaction is of little value for the detection of hydrogenated vegetable oils, while hydrogenated cottonseed oil still responds to Becchi's and Hauchcorne's tests. He also draws attention to a point which must not be forgotten, namely, the ratio of iodine value to refractive index, which is not the same in hydrogenated fats as it is in animal fats.

The estimation of glycerol in hydrogenated fats has been carried out by the ordinary well-known methods by Normann and Hugel,[82] and the results compared with those obtained from the ester values. The dichromate value gives excellent results.

In conclusion, attention may be drawn to the effect of hydrogenation on certain constituents of oils.

1. Hydroxy-fatty acids.—Jurgens and Meigen[83] have studied the behaviour of the hydroxyl group in the presence of nickel. In the case of castor oil, below 200° C., apparently only the double bond is affected, but at higher temperatures the hydroxyl group is more and more rapidly attacked. However, in the case of nickel oxide the hydroxyl group appears always to be more rapidly reduced.

2. The esters of oleic acid and their hydrogenated products have been prepared by Ellis and Rabinovitz,[84] and the characters of the esters and the hardened products determined, using nickel as the catalyst. In most cases the iodine value of the final products was almost negligible, though with ethyl and benzyl oleates and glycerol mono oleate the figure remained in the neighbourhood of 6.

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[79] *Tidskrift Kemi, Farm., og Terapi*, 1916, [20], 285; *J.*, 1917, 603.
[80] *Z. Unters. Nahr. Genussm.*, 1915, **30**, 357; *J.*, 1916, 548.
[81] *J.*, 1914, 1061.
[82] *Chem. Umschau*, 1916, **23**, 45; *J.*, 1916, 932.
[83] *Chem. Umschau*, 1916, **23**, 99, 106; *J.*, 1917, 657.
[84] *J. Ind. Eng. Chem.*, 1916, **8**, 1105; *J.*, 1917, 39.

3. Cholesterol and phytosterol.—Marcusson and Meyerheim[85] have separated the unsaponifiable matter of several natural and hydrogenated fats in order to study the effect of hydrogenation, and as a general rule find that there is less of the sterols in the hydrogenated fats than in the corresponding natural fats, and it would appear that particularly in the case of phytosterol, considerable transformation takes place.

WAXES

Very little work in connection with waxes is on record during the past 12 months.

A paper on the hydrocarbons of beeswax is contributed by Ryan and Dillon,[86] who criticise Buisine's method of estimating the alcohols present by heating with potash and potash lime, on the grounds that some of the alcohols in beeswax are secondary or tertiary alcohols, basing their conclusions on the composition of the hydrocarbons extracted from the product of the above interaction by means of petroleum spirit

The viscosity of beeswax and its possible adulterants, such as carnauba, Japan wax, tallow, spermaceti, paraffin, and ceresin have been determined by Fabris,[87] using nitrobenzene as a comparative substance Considerable divergencies among these substances were observed, and the method is recommended by the author as suitable for analytical work.

The estimation of unsaponifiable matter in waxes is carried out by Wilkie[88] in a somewhat novel manner. He avoids the difficulty experienced in extracting the beeswax after saponification by adding a proportion of castor oil to the beeswax before saponification. A mixture of 0·5 gram of beeswax and 4·5 grams of castor oil is recommended, the total unsaponifiable matter being finally corrected for the castor oil employed.

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[85] *Mitt K Materialpruf*, 1916, **33**, 221 ; *J*, 1916, 549

[86] *Scient Proc Roy Dublin Soc*, 1916, **15**, 107 , *J*, 1916, 971

[87] *Staz Sperim Agrar Ital*, 1916, **48**, 595 , *J*, 1916, 1224

[88] *Analyst*, 1917, **42**, 200 ; *J*, 1917, 723

PAINTS, PIGMENTS, VARNISHES, AND RESINS.

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The year's progress in these industries, as far as can be judged from the published communications and patent literature, is not specially marked. Although there are exceptional papers which show well-tested observations, there appears to be the spirit of stress and hurry which militates against quiet and painstaking progress. America is still the only country where much investigation has been undertaken. The contributors to the American "Chemical Abstracts" have been asked to provide careful and prompt reports in connection with problems for the prevention of corrosion of metals so as to hasten the end of the world-war by acceleration and stimulus of scientific effort. In the British Empire the demands of the war have claimed the energies of the ever-increasing number of chemists. Germany also has fewer contributors.

The search for substitutes is especially noticeable in the German patents, but in this section the success has not been encouraging, and the dearth of the necessary raw materials has not been successfully overcome.

The defect noticed in the last report in reference to the absence of standard methods of testing materials within the British Empire is more and more serious. In these days when materials have to be supplied according to definite requirements, determined occasionally by the results of analyses, it is of the highest importance that standard methods should be laid down by agreement. The connection between properties and composition is becoming more and more recognised, and the call for reports such as those issued by the American Society for Testing Materials is urgent.

The application of physical and chemical methods of investigation requires further extension, so that reliance solely on tests which were the result of experience and skill of the individual workman, but which were incapable of clear expression, may give place to those based on first principles upon which can be built a solid structure capable of firm development and extension.

The properties of varnishes, resins, and paints in their application beyond questions of composition, such as stoichiometry, are essentially the properties of colloids. Already investigators, *e.g.*, Friend, A. P. Laurie, Seaton and his collaborators, recognise the importance of this aspect and endeavour to utilise as far as possible the results obtained from work on allied substances in the elucidation of problems connected with flow, alterations in viscosity, and changes of surface which are not explicable by common chemical causes.

The Properties of Drying Oils.

The contributions to the study of the properties of drying oils are less numerous than last year, notwithstanding the universal demand in connection with material for protective coatings. It is true that in spite of the valuable binding and elastic properties of linseed and other drying oils, their resistance to weathering agents leaves much to be desired. The objection to the want of durability is not so strongly maintained, but as yet no substitute has been found which will combine rapidity of drying with durability. The employment of highly polymerised oils, which are more resistant to weathering agencies and to hydrolysis, is in the opinion of the writer, the direction in which progress is being made.

J. A. N. Friend[1] has studied the effect of heat and oxidation on linseed oil with reference to changes of density, viscosity, and coefficient of expansion. When linseed oil is heated out of contact with air, the density, viscosity, and molecular weight all increase with temperature and length of treatment, but the coefficient of expansion falls steadily. Linseed oil on oxidation loses water, carbon dioxide, and organic vapours, but absorbs oxygen until an equilibrium is reached. The density gradually increases, but the coefficient of expansion falls, the volume increasing up to the setting point of the oil, after which the linoxyn contracts, but the maximum increase in weight (18·57 [illegible]) occurs after the setting point of the oil has been reached. Linoxyn contracts on exposure, probably due to the decomposition of the peroxides. Expansion is dependent on the increase in weight, so that added substances which reduce the maximum increase in weight also reduce the expansion. The contraction suffered by linoxyn explains the cracking of old paint. In the oxidation of linseed oil the methods of determining the drying powers of oils by noting the alteration of weight are merely of comparative value and only serviceable when carried out under precisely similar conditions.

A. de Waele[2] gives a detailed account of the manufacture of linoleum, together with a new method of valuation of the intermediate and finished product, oxidised oil, "cement," &c. The method depends on the resolution of the oxidised oil into three and even four fractions, petroleum ether soluble, ether soluble, and residue ("linoxyn"). The fourth fraction is only of scientific interest.

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[1] *Chem. Soc. Trans.*, 1917, **111**, 162; *J.*, 1917, 462

[2] *J. Ind. Eng. Chem.*, 1917, **9**, 1; *J.*, 1917, 149

A comprehensive series of tests made on eight representative samples of linoleum, and from different materials including China wood oil, shows good agreement between the valuation as carried out in the laboratory and practical wearing tests. The use of China wood oil as a substitute for Kauri gum is shown to be detrimental to the quality of the finished article. The mechanism of the chemical changes occurring in the oil during oxidation is discussed, and an hypothesis is formulated as to the identity of the fractions, which is supported by elementary analyses. The four fractions obtainable consist of mixed glycerides in increasing order of oxygen content, saturation by oxygen of the various acid radicles in the glycerides being according to the scheme L_2O_6, one double bond being left untouched (oleic acid radicle suffers no change and linolenic acid forms a diperoxylinolenic acid).

A comparison is given between the properties of linoxyn and "cyclolin," the former being solid oxidised oil and the latter solid polymerised oil. Cyclolin is difficult to saponify and insoluble in amyl alcohol, and is considered by de Waele to be of a ring structure. Linoxyn is soluble in amyl alcohol, so that a separation of the two substances is obtainable.

In view of the complexity of composition of raw linseed oil and the formation and existence of many mixed glycerides as indicated by Morrell, it would seem advisable to investigate the simpler cyclolin from wood oil.

Krumbhaar[3] states that the speed of polymerisation constitutes the greatest difference in the behaviour of Chinese wood and linseed oils, and agrees with Fahrion and others, that the polymerisation product is partly soluble in the unchanged oil and the viscosity increases with the amount of polymer until the saturation point is reached, when the polymer is thrown out. He notes the effect of acids in retarding the formation of gels, and observes that if the acids are removed from linseed oil by heating *in vacuo*, the mass stiffens in **3–4** hours just like wood oil.

C. D. Holley and J. P. Roberts[4] have investigated the "turning point" of a large number of samples of Chinese wood oil, and find evidence of considerable adulteration, although an oil of the highest purity is occasionally obtainable from Chinese merchants.

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[3] *Chem.-Zeit.*, **40**, 937–8; *J.*, 1916, 1225.

[4] *Drugs, Oils, and Paints*, 1917, **32**, 263.

The scarcity of drying oils in Europe has led to the employment of many substitutes, but most are very dark in colour, thin and rapid drying giving a lustreless non-durable coat, and the colour darkens with age.[5]

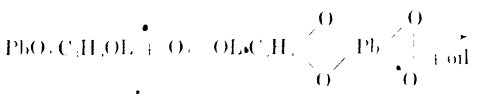
W. McD. Mackey and H. Ingle[6] have compared the times in which oiled cotton wool attained a temperature of 200° C. in the cloth oil tester[7] when linseed oil was oxidised in the presence of soluble metallic catalysts. The driers used were the metallic soaps of Co, Mn, Ce, Pb, Cr, Fe, U, Na, Bi, Ag, Zn, Th, Hg, and Al. The metals which were most active were those which could exist in more than one state of oxidation provided the salts of the lower oxides were more stable than those of the higher forms. Sodium acts as a more active catalyst than was to be expected. Generally the order of activity was according to the list given above. In the case of copper, the metal accelerates and then retards the oxidation of both linseed and olive oil. With the exception of the Na, Bi, and Hg soaps of olive oil, all the soaps of both linseed and olive oil fired oiled cotton wool on standing in the air. In all cases, with the exception of Cu and Sn, it was found that the introduction of a metal in oil-soluble form accelerated the increase of temperature, *i.e.*, the oxidation of the oil. The mode of comparison is novel and the results are interesting as confirming the work of other investigators in many directions.

The comparative inactivity of thorium is noticeable because from the writer's experience a cerium drier containing other rare earths shows an improved accelerating effect. The exceptional position of sodium may be connected with a heat change consequent on polymerisation which may be accelerated by the presence of more electropositive metals. From the list given, Mackey and Ingle state that the more oxides a metal can form the greater will be its catalytic power—a statement which must be accepted with reserve.

H. Ingle[8] discusses the mechanism of the action of metals as driers, taking lead as a type. When lead oxide is heated with linseed oil the action is said to proceed according to the following scheme:—

$$C_3H_5(OL)_3 + 2PbO = PbO.C_3H_5(OL) + Pb(OL)_2$$

Glyceryl plumbolinoleate   lead linoleate



$$PbO.C_3H_5(OL) + O_2 = OL.C_3H_5\begin{smallmatrix}O\\ \\ O\end{smallmatrix}Pb\begin{smallmatrix}O\\ \\ O\end{smallmatrix} + \text{oil}$$

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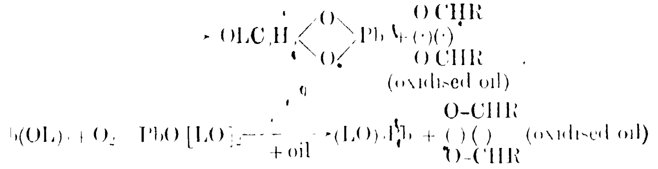
[5] *Farben-Zeit.*, 1916, **22**, 158.

[6] *J.*, 1896, 40.

[7] *J.*, 1917, 317.

[8] *J.*, 1917, 319.

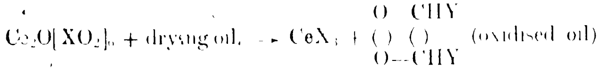


The glyceryl plumbolinoleate and lead linoleate undergo oxidation cording to the above scheme, being subsequently reduced, and the tion continues; and provided the metal remains in solution as a soap e oxidation of the oil proceeds.

Morrell[9] has described a number of cerium salts of unsaturated acids btained from drying oils. The absorption of oxygen by cerium -elaeostearate has been studied. The conclusion drawn is that the erium salt (soluble in ether) is first oxidised to a basic ceric salt soluble in ether of the type Ce_2OX_6 which further absorbs oxygen to ive a salt of the type $Ce_2O[XO_2]_6$.

The action of cerium salts as driers can be expressed as follows.

$$CeX_3 \text{ or } Ce_2OX_6 \rightarrow Ce_2O[XO_2]_6$$



$$Ce_2O[XO_2]_6 + \text{drying oil} \rightarrow CeX_3 + \begin{matrix}O-CHY\\ | \quad\ \ | \\ O-CHY\end{matrix} \quad \text{(oxidised oil)}$$

F. Fritz[10] proposes to use in paints linoxyn dissolved in benzine, vith the addition of boiled oil, and shows[11] that linoxyn solutions may e substituted for boiled oil. In this case the linoxyn is first melted vith resins, whereby it is made soluble, and then benzene added as hinner. Damar and copal resins may be used and rosin oil is well-uited as a vehicle.

C. D. Holley and J. P. Roberts[12] have examined samples of Chinese wood oil from nuts grown in the Southern States of the U.S. and rom California.[13] All the oils were pale in colour, and, except in the ase of two from California, gave normal constants. Practical tests indicated that they are similar to genuine Chinese wood oils and are superior to recent commercial shipments of the latter. The California nuts were grown under semi-arid conditions, but it is uncertain whether climatic conditions caused the abnormal oils.

A paper of the Bureau of Plant Industry, which has not been available to the public, gives general information on the habitat, conditions for growth, and growing experiments in the U.S. of the tung oil tree.[14]

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[9] *Chem. Soc. Trans.*, 1918, **113**, 111; *J.*, 1918, 130 A.

[10] *Chem. Umsch. Fett. Harz. Ind.*, **23**, 29-30.

[11] *Ibid.*, p. **43**.

[12] *Drugs, Oils, and Paints*, **1917**, **32**, **415**

[13] *See Annual Report*, Vol. I., p. 183.

NATURAL RESINS, COLOPHONY, ESTER GUMS, AND TURPENTINE

The scarcity of the natural lacquer of the Japanese, the sap of *Rhus vernicifera* has brought to notice "Thitsi," a similar product obtained from the black varnish tree, *Melanorrhoea usitata*. It has been found to be equal to Chinese lacquer although slower drying. It shows advantages over Japanese lacquer, but the conditions required for its slow hardening will prevent it finding favour as a substitute for other materials drying more quickly. Even if these disadvantages were overcome, it appears unlikely that thitsi will be extensively exported for use in Europe.

L. Paul has continued his investigations on the properties of colophony and its ammonium salts.[15] Unchanged γ-pinic acid (m. pt. 74–76° C.) can be separated from colophony by treatment with very dilute ammonia and alcohol because of the ease with which its ammonium soap is decomposed, whilst the α-pinic acid can be obtained from the filtrate on acidification. γ-Pinic acid gradually changes to α-pinic acid and α-pinic acid into β-pinic acid. The autoxidation of colophony is comparable with the transformation of α-pinic acid into β-pinic acid. γ-Pinic acid after standing for a considerable time does not give the γ-pinic acid ammonium soap but is changed to β-pinic acid.

The action of nitric acid on colophony is similar to that of exposure to air. Cold alcohol with colophony yields sylvic acid, while hot alcohol yields γ-abietic acid.

As a means of classifying resinous substances solubility in petroleum is suggested, *e.g.*, γ-pinic acid, sylvic acid, γ-abietic acid are soluble, whilst α- and β-pinic acids are insoluble.

C. G. Schwalbe[16] finds that ether extracts better resin from fir and pine than does alcohol, the latter yielding almost brittle resins. Steam distillation of the resins yields no turps, but turps can be obtained when the fresh or extracted wood is heated with caustic soda under pressure at 170° C.

A synopsis of the properties and constants for valuation of copals is given.[17]

Gums or gum resins from plants of the genus *Xanthorrhoea* are the subjects of three patents by H. C. Miller and H. A. Irlam.[18] The first patent is for the purification of blackboy gum, the second is for the preparation of picric acid and other nitrophenols by treatment with nitric acid, while the third deals with the extraction of dyestuffs from the gums.

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[14] *Drugs, Oils, and Paints*, 1917, **32**, 443.

[15] *Seifenfabr.*, 1916, **36**, 545; *J.*, 1917, 537.

[16] *Z. Forst- u. Jagdwesen*, 1916, **92**; *J.*, 1917, 395.

[17] *Ind. Quim.*, 1916, **13**, 266.

A. W. Schorger,[19] in continuation of his investigation on the oleoresins of *Coniferæ*, has examined the oleoresin of the heart wood of Douglas fir and found it to have a rotation of + 2·84° and to consist chiefly of a *l*-pinene (17·52°), doubtless identical with the fir pinene of Frankforter and Frary.[20] From the sapwood of Douglas fir a 22% yield of volatile oil was obtained containing *l*-pinene (18·96°) giving a nitrosochloride.

D. E. Tsakalotos[21] refutes the statements of Gildemeister[22] that the buds of the Aleppo pine (*Pinus Halepensis*) consist largely of *l*-pinene, and demonstrates that *d*-pinene is the variety found which is independent of the locality of growth or part of the plant, and that it is the principal constituent of the essential oil of the pine. *Pinus maritima* of France, Spain, and Italy contains *l*-pinene.

O. M. Halse and A. Dedichen[23] give a method for the recovery of oil of turpentine in the digestion of sulphate wood pulp. In the manufacture of wood pulp by the sulphite process a volatile oil is obtained with mercaptan-like odour, and from which an oil similar to ordinary turpentine is obtained. The yield is 1–1·5 kilos. for spruce and 10 kilos for pine wood per ton of cellulose. The purified oil consists chiefly of α-pinene, with small quantities of β-pinene which gives no pinic acid on oxidation and is dextrorotatory, whereas the natural oil gives a *l*-variety.

E. R. Besemfelder[24] claims that in his process for the artificial seasoning of wood, Germany could be rendered independent of imported rosin and turpentine. Presumably trichloro-ethylene is employed as solvent for the resins and the extract varies with the origin. fir yields 1 extract, of which half consists of rosin and turpentine and the remainder of fat (mainly compounds of oleic acid). The value of the resinous extract from German wood would amount to £6,000,000 annually. Sawdust or wood to be extracted by this process must be treated as soon as possible because the solubility of the rosin decreases on exposure owing to oxidation. The relative cost of the process is not given. The extraction process as outlined is stated to prevent the blue discoloration responsible for a considerable loss of timber in the ordinary seasoning process.

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[18] Eng. Pats. 103006 (1916), 104352 (1916), and 104353 (1916); *J.*, 1917, 395, 499, 500.

[19] *J. Amer. Chem. Soc.*, 1917, **39**, 1040; *J.*, 1917, 724.

[20] *J.*, 1906, 1107.

[21] *Gaz. Chim. Ital.*, 1917, **47**, i, 285; *J.*, 1917, 930.

[22] "Die aetherischen Oele."

[23] *Ber.*, 1917, **50**, 623; *J.*, 1917, 658.

[24] *Chem.-Zeit.*, 1916, **40**, 997; *J.*, 1917, 148.

M. Palazzo[25] has compared the pinenes obtained from the Italian *Pinus pinaster* and *pinea* with the oils of the same trees grown in France. The Italian oil gives a *l*-pinene with a slightly higher optical rotation.

A. P. Laurie and Clerk Ranken[26] describe the imbibition exhibited by some shellac derivatives. The solid which separates on cooling a solution of shellac in boiling sodium carbonate, when immersed in cold water, expands rapidly and ultimately disintegrates to a flocculent precipitate. At the maximum point of expansion the solid on immersion in strong sodium carbonate solution contracts, expanding again when transferred to water. It was found that the expansion was inversely proportional to the concentration of the salt solution. The differences between the behaviour of this compound and substances of a colloid nature are largely explained by the insolubility of the soluble portion in strong salt solutions.

Since the shellac molecule is permeable to salt molecules, the mechanism of the expansion may be accounted for by the passage of the salt through the diaphragm, the soluble nucleus dissolving in the presence of the salt solution, and the amount that can dissolve controlling the consequent osmotic pressure.

THE PROPERTIES OF PIGMENTS.

L. Bock[27] reviews the properties of the various basic zinc chromates and the alkali zinc chromates described in the literature with reference to the use of zinc yellow in the pigment industry. In another communication[28] the same author states that Egyptian blue or Vestorian blue is only of historical interest; it was manufactured by Deschamp Freres and its formula is given as $CaO,CuO,4SiO_2$.

The theory of colour lakes is discussed by O. Baudisch[29] in reference to the lake-forming azo dyestuffs in their relation to Werner's theory of mordants.[30] According to this theory, the colour lakes belong to the class of metal complex salts and the lake forming dyestuffs are characterised by the presence of salt-forming groups, and groups capable of forming a co-ordinate combination with the metallic atom so that an internal complex salt can result. The *o*-hydroxyazo dyestuffs are typically mordant dyestuffs conforming to this rule. Naturally the introduction of substituent groups plays a most important part in the lake-forming properties: moreover the introduction of side chains is able to bring in spare valencies which have a strong influence. The influence of side chains in the ortho-position to the azo-nitrogen is greater than in the meta- and para-positions. The methyl group in the ortho-position is antagonistic to lake formation, while the sulphonic group in the ortho-position is favourable. In the anthraquinone series Werner's theory is consistent with the observation that the most valuable lake-forming dyestuffs are those containing meta- and ortho-hydroxyl groups in positions contiguous to each other.

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[25] *Annali Chim. Appl.*, 1917, 7, 88; *J.*, 1917, 463.

[26] *Roy. Soc. Proc.*, 1917, A, 94, 53; *J.*, 1917, 1242.

[27] *Kolloid Z.*, 1917, 20, 145.

[28] *Z. angew. Chem.*, 1916, 29, 228.

[29] *Z. angew. Chem.*, 1917, 30, 133; *J.*, 1917, 705.

[30] *J.*, 1908, 439.

The Badische Anilin und Soda Fabrik[31] have patented the process of manufacture of a bright red pigment insoluble in water and oil, very fast to light and not affected by water or lime; the diazo compound of 1-aminoanthraquinone is combined with 1-benzoylaminohydroxynaphthalene, with or without the addition of Turkey-red oil.

A number of patents have been granted for titanic oxide pigments;[32] the specifications consist in descriptions of different modes of incorporation of titanic oxide into pigments, or into linoleum, together with process for obtaining titanic oxide from materials containing it. The introduction of an oxide of a rare metal is of interest as the popularity of rare earth oxides is likely to increase, owing to their general stability and refractory characters, if they are obtainable in sufficient quantities.

H. E. Merwin[33] describes a litharge-glycerol cement employed for lining digesters used in the manufacture of sulphite pulp. Litharge and glycerol form a crystalline compound which cements the grains of unattacked litharge. The crystals are stated to consist of 95 % $C_3H_4O_2,PbO$, plus 5 % lead. This combination of glycerol and lead oxide is of some interest in connection with the properties of natural and artificial glycerides.

W. Gallenkamp[34] states that when ordinary water-glass paints are mixed with sodium bicarbonate shortly before use, whereby carbon dioxide is evolved and silica precipitated, a more viscous material is produced owing to the separation of silicic acid, so that the paint becomes waterproof and weatherproof within 12 hours of its application.

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[31] Ger. Pat. 297411, 1914; *J.*, 1917, 639.

[32] L. E. Barton, U.S. Pats. 1205144, 1218161, 1223356, 1234260, 1235638, 1236655; *J.*, 1917, 91, 463, 659, 1019, 1047, 1055; L. E. Barton and H. A. Gardner, U.S. Pat. 1236367; *J.*, 1917, 1019; H. A. Gardner, U.S. Pat. 1216980; *J.*, 1917, 463; H. Wade, Eng. Pat. 108805; *J.*, 1917, 1055; A. J. Rossi and C. H. Schreder, U.S. Pat. 1205267; *J.*, 1917, 91.

[33] *J. Ind. Eng. Chem.*, 1917, **9**, 390; *J.*, 312.

[34] Ger. Pat. 294330, 1916; *J.*, 1917, 395.

The importance of preservative coatings for iron and steel is the subject of a review by L. P. Nemzek[35]. He gives specifications for a satisfactory basic lead chromate paint which is recommended as superior to all others for the priming coat. It should consist of 75% of basic lead chromate and 25% of a chemically inert pigment such as asbestine in a vehicle consisting of 90% of pure linseed oil and 10% of combined thinner (volatile) and drier. The complete paint weighs 12·5 lb. per. gall.

In an anonymous paper[36] the action of heat on ochres is described. The colours of the red varieties, which occur sparingly compared with the yellow varieties, are not so rich as those obtained by calcining the latter. The quality depends not only on the composition but also on fineness, plasticity, and fusibility. Between 100–250° C. the colour gradually changes to yellowish-brown, and at 250° C. suddenly becomes red. The best yellows do not always produce the best reds, the length of heating and rate of cooling influencing the final shade, but all shades produced by calcination are stable. Further heating to 700–800° C. gives a reddish-purple ochre, but if the mass is gradually heated to above 950° C. it reverts to its original yellow colour, but with different properties; this variety is obtained only within narrow temperature limits of about 50° C., as further heating causes the ochre to blacken. At 1200° C. the ochres fuse to a spongy mass, and at 1600° C. they give a black vitrified substance hard enough to scratch glass.

J. S. Harris and M. Y. Seaton[37] discuss the conditions of grinding of pigments and the relative merits of the steel roll and stone type of mill for various grades of work. They state that the consistency of the paste has a marked effect on the grinding efficiency. For pigments ground in oil the addition of blown linseed oil or of refined oil with a high acid value, or a mixture of these depending on the pigment, results in increased grinding efficiency. For pigments ground in japans or varnishes a vehicle of proper surface tension and drying characteristics should be selected.

A. H. Sabin[38] gives a clear account of the advantages of painting steel structures, the merits of red lead, formulae for mixing paints, preparing iron surfaces preliminary to painting, and the number and kinds of coats to be applied.

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[35] *Drugs, Oils, and Paints*, 1916, **32**, 191.

[36] *Drugs, Oils, and Paints*, 1916, **32**, 167.

[37] *Drugs, Oils, and Paints*, 1916, **32**, 192.

[38] *Elec. Age*, 1917, **50**, 35.

The preparation of metals for painting is the subject of several patents in which phosphates are the main ingredients; *e.g.*, Gravell and the American Chemical Paint Co.[39] recommend the cleaning of the metallic surface with solutions of ortho-, pyro-, and meta-phosphoric acids, followed by a relatively weak solution of ortho-phosphoric acid.

A. G. Betts[40] uses anhydrous barium phosphate as a pigment to give with drying oils a paint which dries with a glossy surface.

The examination of the pigments of copying-ink pencils is the subject of a paper by C. A. Mitchell.[41] He finds the proportion of dyestuff (usually methyl violet) ranges from 21 – 50 , with varying proportions of graphite and kaolin clay.

SYNTHETIC RESINS.

The number of patents[42] for processes for the manufacture of synthetic resins is still on the increase. Many appear to be modifications of the older schemes involving the condensation of an aldehyde with a phenolic derivative by means of a suitable condensation agent. The variety of the patented methods may be judged from the following examples of substances which it has been proposed to use: condensation product of ketones with a cresol or substances of the type $R_2C(C_6H_4OH)_2$, with compounds containing at least one methylene group; monochlorophenols; condensation products of phenols in the presence of ammonium salts of sulphoacids and of an acid which does not decompose such salts.

Resins made on the general plan are compounded or embodied during the process of preparation with a variety of substances, *e.g.*, carbohydrates, albuminous materials, tannins, sulphonated resin oils, cellulose esters, a chlorinated hydrocarbon solvent, and cumarone resins.

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[39] U.S. Pat. 1211138, *J.*, 1917, 223; Eng. Pat. 107921, 1916.

[40] U.S. Pat. 1213330, *J.*, 1917, 395.

[41] *Analyst*, 1917, **42**, 3; *J.*, 1917, 147.

[42] A. L. Brown, U.S. Pat. 1212738, *J.*, 1917, 396. L. Behrend, U.S. Pat. 1214414, *J.*, 1917, 347. J. W. Aylsworth, U.S. Pat. 1197171, *J.*, 1916, 1071. L. H. Baekeland and A. H. Gotthelf, U.S. Pat. 1217115, *J.*, 1917, 463. L. Behrend, Eng. Pat. 105295, *J.*, 1917, 969. K. Tarassoff, Eng. Pat. 102751, *J.*, 1917, 150; U.S. Pat. 1235507, *J.*, 1917, 1010. K. Tarassoff and P. Shestakoff, Eng. Pat. 104887, *J.*, 1917, 558. L. V. Redman, U.S. Pat. 1209333, *J.*, 1917, 225. B. B. Goldsmith, U.S. Pat. 1228428, *J.*, 1917, 894. W. B. Jones, U.S. Pat. 1209165, *J.*, 1917, 225. C. P. Steinmetz, U.S. Pat. 1215072, *J.*, 1917, 396. W. A. Beatty and G. W. Beadle, U.S. Pat. 1225748, *J.*, 1917, 724. W. A. Beatty, U.S. Pats. 1225748, 1225749, 1225750, *J.*, 1917, 724. A. W. C. Van Verhout, Eng. Pat. 118041, *J.*, 1917, 1185. L. V. Redman, A. J. Weith and F. P. Brock, U.S. Pats. 1242592, 1242593, *J.*, 1917, 1242.

Resins soluble in spirit solvents are described, as well as the harder and infusible varieties. In one patent a liquid coating composed of a phenolic condensation product with Chinese wood oil and a drier is described, but it is pointed out that the drying oil must be in excess.

The cumarone and para indene resins, which were stated in the last Annual Report to have attracted considerable interest in Germany, are in the opinion of Krumbhaar[43] unsatisfactory The cumarone varnishes are tacky, and although they can be hardened by the addition of para-indene yet the durability is poor Moreover unaccountable thickening of mixtures occurs when cumarone varnishes are mixed with certain pigments.

Further information respecting the properties of polymerised acrylic esters is given by O Röhm[44]

The acrylic acid esters are prepared from glycerin, lactic acid, etc and when exposed to ultraviolet light or sunlight, polymerise to hard, varnish-like, elastic masses. They are soluble in solvents for oils, and are stated to dry rapidly and not to be readily affected by exposure or by many chemical agents. The polymerisation of organic vinyl esters to reproduce varnishes is completed in the material impregnated.[45]

PROPERTIES OF VARNISHES.

The importance of the study of viscosity of varnishes is illustrated in a paper by M F Seaton, E T Probeck, and G B Sawyer, who have continued their investigations on the physical analysis of varnishes (see Report, Vol I., 194) They have determined the viscosities of varnishes by means of the Doolittle viscometer, and find that the changes which occur in the viscosity during ageing or on the addition of certain solvents are due to change in the character of the colloids present Valuable information can be obtained as to the nature of a varnish by plotting the results of the viscosity changes at different temperatures, and moreover the results are in keeping with hypothesis. They find that with stable varnishes the viscosity becomes approximately constant after a month, whereas if it continues to rise materially after that time, it will continue doing so until the varnish is useless. Varnishes of the true solution type (gum with little polymerised oil) show curves of variation of viscosity with temperature similar in form to but quite distinct from the curves of varnishes of the emulsoid type, which are practically straight lines. By plotting the results of the viscosity obtained at different temperatures it is often possible to obtain information as to the nature of the varnish. Seaton states that the addition of an active thinner to a colloidal varnish will change the viscosity from a straight line to a curve relationship

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[43] *Farben-Zeit*, 1916, 21, 1086, *J.*, 1917, 395

[44] Ger Pat 295340, 1916, *J.*, 1917, 296

[45] *Chem Fabr Griesheim-Elektron*, Ger Pat. 291299, *J.*, 1916, 698

A method of determination of viscosity applicable to varnishes is given by A. L. Feild.[46] It is based on the fact that when the outer of two coaxial cylinders separated by a liquid is rotated at a constant angular velocity, a torque proportional to the viscosity of the liquid is exerted on the inner cylinder. The torque can be accurately measured, and the results may be expressed in terms of specific viscosity referred to that of water, or in absolute units.

No publications on questions of blooming or cracking of varnished surfaces have been observed. In this connection it may be of interest to note that the so-called pinholey structure would appear (from observations of the writer of the report) to be connected with the presence of globular masses of emulsoid material around which the medium has flowed on setting, leaving peculiar depressions. These masses can be observed by flatting any surface showing pinholes on glass.

The theory and practice of wood colouring are discussed by F. Moll,[47] Wood colouring resembles wood impregnation on the one hand and textile dyeing on the other. Water is the only solvent for thorough colouring. The greater the molecular weight of the dye and the greater the predominance of colloidal properties, the less the diffusion but the greater the fastness to light and water.

G. H. Hadfield and A. E Bawtree have patented[48] the production of decorative surfaces with China wood oil, varnishes depending on the use of nitric acid vapours or the equivalent (*i.e.*, any gas capable of modifying colour, hardness, or structure of a varnish except that from an internally heated gas oven).

The heating of metal which has been japanned by the passage of an electric current resulted in better surfaces than by ordinary stoving; moreover, stoving by radiation is stated to give better results than by convection currents. Details of the stoves are given in the case of the radiant heating, but the electric heating direct has not been sufficiently developed.[49]

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[46] *U S. Bureau of Mines* (1917), *Technical Paper*, 157, *J*, 1916, 1237.

[47] *Z. angew. Chem.*, 1916, **29**, 405-8; *J.*, 1917, 132.

[48] Eng Pat. 109657, 1916; *J*, 1917, 1139.

[49] W. S Scott, *Elec. J*, 1917, **14**, 252-4.

The Report of the Committee D1 on preservative coatings for structural materials (P. H. Walker and others)[50] is of great practical value as shown by the subjects which have been investigated. Sub-committee 3 on testing of paint vehicles (H. A. Gardner) includes an investigation on tests for the purity of Chinese wood oil and on the use of perilla oil in paints, varnishes, linoleums, etc. Sub-committee 5 on linseed oil (G. H. Pickard and others) gives results and comments of analysts on samples of raw and boiled oils from Argentine seeds. Sub-committee 8 deals with the methods of analyses of paint materials (G. W. Thompson), and suggests methods for routine analysis of white pigments, while another Sub-committee (11) deals with paint thinners other than turpentine. Sub-committee 13 deals with shellac (Langmuir), while Sub-committee 14 deals with the preparation of iron and steel surfaces for painting, and gives procedure for conducting tests (A. W. Carpenter).

In the opinion of the writer the full statement of the scope of the work undertaken is of importance as showing the great advantage which would accrue to the British industry if a similar society were established in this country.

ANALYSIS AND APPARATUS.

In connection with spirit varnish analysis mention must be made of the determination of precipitation points[51] on addition of known quantities of water; this is of considerable use in the examination of shellac varnishes for impurities such as rosin and spirit-soluble gums. The point of precipitation is determined by appearance of turbidity and the Tyndall effect. Generally the smaller the amount of water added to produce precipitation, the higher the proportion of soluble copal, while rosin and accaroid follow in decreasing order of precipitation power. The results appear in the reviewer's experience to be worthy of consideration.

The errors in determination of acid values of boiled oils and varnishes are pointed out by E. E. Ware and R. E. Christman.[52] The lead, manganese, cobalt, and zinc salts of drying oils are almost completely hydrolysed in the determination of acid values, so that in varnish analysis this factor must not be neglected.

A rapid and accurate method of determination of volatile thinners in oil varnishes is described by A. de Waele and F. Smith.[53] The results obtained are usually 1·5 % lower than those given by McIlhiney's method.

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[50] *Proc. Amer. Soc. Testing Materials*, 1916, **16**, 270.

[51] H. Wolff, *Farb.-Zeit.*, 1916, **21**, 1, 198.

[52] *J. Ind. Eng. Chem.*, 1916, **8**, 996; *J.*, 1916, 1225.

[53] *Analyst*, 1917, **42**, 170; *J.*, 1917, 603.

The extension of the Liebermann-Storch reaction to copal resins and damars is described by R. E. Jameson.[54] The colours are essentially different shades of brown and wine red, and are in the writer's opinion not so characteristic as the deep violet colour given by colophony.

H. Wolff[55] has investigated the methods of analysis of wood oil varnishes. He states that McIlhiney's method for detection of tung oil in varnishes in the presence of resins is not satisfactory, especially in mixtures in which the tung oil has been heated. The tung oil acids from untreated oil are found to be practically completely esterified by the author's method, so that they can be estimated after separation of the resin acids.

F. M. Lidstone[56] describes a simple form of viscometer useful for determining the viscosity of an oil when only small quantities are available. It consists essentially of a fine capillary which has a cup at the top to hold the oil, a small bulb blown in it in the middle, and a stop-cock at the bottom, the whole being surrounded by a water-jacket. After a steady temperature is reached the stop-cock is opened and the time taken for the bulb to become full of oil is noted; the time taken by the mercury flowing freely is also noted. The disadvantages of an exposed jet and wide orifice are avoided, the instrument is very rapidly cleaned, and the viscosity in absolute measure can be obtained by this instrument with a much nearer approach to accuracy than with most commercial viscometers.

Mention may be made of the description of electrically-heate drying ovens or stoving ovens for paints, varnishes, japans, and enamels. W. J. Scott[57] states that any suitable number of units of the ribbon type heaters of 2·5 kilowatts at 120 volts may be installed. A installation consists of one or more heaters connected with a two-wir circuit controller by a knife switch; a three-wire single phase or eve a three-phase circuit may be used. Details are given in the paper fo fitting up the ovens controlling the temperature so as to ensure safet of working.

The author desires to express his thanks to Mr. P. J. Fay, M.A., fo valuable help in the selection and arrangement of the material for thi report.

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[54] *J. Ind. Eng. Chem.*, 1916, **8**, 855; *J.*, 1916, 1071.

[55] *Farben-Zeit.*, 1916, **21**, 1302.

[56] *J.*, 1917, 270.

[57] *Elec. J.*, 1917, **14**, 252.

INDIARUBBER, ETC.

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Research in the rubber industry has been very active since the issue of the last Report, witness the numerous papers published in our own Journal. These mostly deal with the preparation of plantation rubber and the principles of evaluation. The users of raw rubber, that is, the manufacturing industry, have not been able, or have not thought fit, to lay down principles for the guidance of the plantation industry; nor are they agreed as to the preferred qualities of plantation rubber, except in the matter of uniformity of rate of cure. Consequently much of the recent research deals directly or indirectly with this subject. At present, data is being accumulated at rather a rapid pace and differences of opinion exist as to the interpretation to be placed on the results. The situation as it stands is summarised in the present Report, and in one instance a detailed reference is made to earlier work for the sake of stating the position as clearly as possible.

STATISTICS

The world's output of crude indiarubber for the last three years is summarised by Lewis & Peat[1] as follows:

	1914	1915	1916	1917
	Tons.	Tons.	Tons.	Tons
Plantation Para ...	64,500	96,000	150,000	215,000
Wild Para	36,800	37,000	37 250	38,900
Other sorts... ...	14,350	13,000	14 750	12,000

It will be noted that the output of wild Para (mainly Brazilian) and other sorts remains remarkably constant, while the output of plantation Para (from the East) continues to increase rapidly. In 1915 the latter amounted to two-thirds of the total, and for 1916 almost three-quarters (74%) of the total. As this rubber is almost entirely clean and dry, while wild Para contains 20 of moisture and other sorts frequently more, it will be noted that the output of plantation considerably exceeds three-quarters of the total world's output reckoned dry. The increase in rate of output of plantation rubber shows no sign of diminishing to date, as from the above figures it appears that the 1915 output showed a 19 increase on the 1914 output, that for 1916 showed a 56 increase on the 1915 output and that for 1917 a 13 increase over 1916

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[1] *Plantation and Wild Para Rubber Report and Statistics.*

PREPARATION OF PLANTATION RUBBER

Various papers have been published by the research organisations working with a view to improving the quality and uniformity of plantation rubber These organisations include the Imperial Institute in conjunction with the Agricultural Department of Ceylon; the Federated Malay States Government Agricultural Department at Kuala Lumpur, and the Dutch Government Research Stations in the Island of Java The Rubber Growers' Association has proceeded with the work of systematising the methods of working on estates, and has revised its tables of recommendations for the preparation of sheet and crêpe rubber The Association has also published a pamphlet giving fuller details in elaboration of the above-mentioned tables[2] based on information supplied by its scientific staff

As regards recent research work, attempts have been made to separate rubber of different properties by fractional coagulation of latex with acetic acid. Experiments in Ceylon[3] led to negative results, but de Vries[4] finds that the first clot, amounting to 15 25 of the total rubber, separated by means of acetic acid, consists of a yellow to dark brown rubber of high viscosity, high rate of vulcanisation, and low tensile properties The writer has observed the separation of a similar yellow rubber known in Ceylon as "butter rubber," but the latex yielding this rubber appeared to be abnormal and contained minute clots

According to Campbell,[5] coagulation with the minimum proportion of acetic, formic, sulphuric, and hydrofluoric acids (0·13, 0·07, 0·10, and 0·01 part of the acids respectively per 100 c.c. of latex) produced rubber showing the same tensile properties and rate of cure. Also the addition of small quantities of ammonia (0·0056), sodium sulphite

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[2] *The Preparation of Plantation Rubber*, May, 1917.

[3] *Bull Imp Inst*, 1916, **14**, 60-64

[4] *Archief voor Rubbercultuur in Ned Indie*, 1917, **1**, No 3, *J*, **1917**, 1104.

[5] *Bull. Dept. Agric, Ceylon*, No. 23, 1916; *J.*, **1916**, 1226.

(0·2), and formaldehyde (0·5) were without influence on the results. On doubling the proportion of acid, the rate of cure was unaffected, except in the case of sulphuric and hydrofluoric acids. On the other hand, de Vries[6] finds an appreciable reduction in rate of cure by increasing the proportion of acetic acid to four times the original quantity, which confirms Eaton and Grantham's earlier results. It seems to be generally admitted that acetic acid is the most satisfactory coagulant hitherto examined, and that it is preferable to sulphuric or hydrofluoric acid, particularly as an excess of the latter is more likely to have an adverse effect on the rubber.[7]

The influence of rolling on crêpe rubber has been investigated,[8] and it is found that a moderate amount of extra rolling has no appreciable effect on the tensile properties, viscosity, or rate of vulcanisation as long as the rollers are kept cool. On the other hand, with pronounced over working, a slight increase has been noted in the time required for vulcanisation.[7]

A recommendation has been made[9] to add an alkaline solution of creosote to the latex before coagulation. It is stated that this does not in any way affect the properties of dry sheet rubber, and, in the case of rubber allowed to remain wet after coagulation, the resulting slab or block "appears to have invariably a short time of vulcanisation and to give very good mechanical results after vulcanisation."[10] The previous work of Whitby, Eaton and others on the effect of smoking and creosote led to the conclusion that these agencies had a tendency to retard the rate of cure of the rubber produced. It would therefore appear that the short time of vulcanisation referred to must be ascribed to the alkali added with the creosote. The effect of alkalis in promoting vulcanisation will be referred to later.

Experiments have also been made on the various methods of drying rubber in air at ordinary temperature, in hot air, or in a vacuum drier, and the general conclusion seems to be that these modifications in procedure do not appreciably affect the tensile figures or time of vulcanisation of the rubber.[10]

Two or three papers have been published dealing with the spontaneous coagulation or natural clotting of *Hevea* latex. Campbell[11] finds that calcium chloride facilitates the spontaneous coagulation, as also do barium chloride and magnesium sulphate to a lesser extent. It would, however, appear that barium chloride is practically as efficient as calcium chloride if equimolecular quantities be taken. The author has further experimented, removing the lime salts which are naturally present in the latex by means of neutral potassium oxalate or sodium fluoride, and finds both these salts have an inhibitory effect. Sodium fluoride may have an inhibitory action on the coagulating enzyme, on the assumption that spontaneous coagulation is brought about by an enzyme. Latex allowed to coagulate spontaneously develops considerable acidity. This acidity has been shown to be due to bacterial action, and consists almost entirely of lactic acid. Denier and Vernet[12] made a bacteriological study of the coagulation of latex and isolated a bacterium which they find to be invariably present. This bacterium when introduced into latex produces coagulation in 24 hours. However, it is well known that latex put aside often coagulates completely or almost completely of itself within this period. Much depends on the shape of the vessels in which the latex is coagulated. The authors also state that the addition of sugar accelerates the action. The use of sugar for coagulation of latex was referred to in the last report, p. 199. The process of spontaneous coagulation with exclusion of air has been patented.[13] In the specification it is claimed that coagulation is complete within 24 hours without addition of any acid or other coagulant. It is also claimed that the coagulum is practically free from discoloration and devoid of unpleasant smell. The latex is coagulated in a suitable trough or pan, which is fitted with a lid the air being excluded by means of a water seal running round the edge of the vessel. The use of sugar is also referred to by O. de Vries,[14] who finds only a very slight difference in quality between rubber coagulated spontaneously with the addition of sugar and that coagulated with acetic acid.

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[6] *Archief*, 1917, **1**, No. 1; *J.*, 1917, 1140.
[7] *Bull. Imp. Inst.*, 1916, **14**, 564; See *J.*, 1917, 604.
[8] O. de Vries, *Archief*, 1917, **1**, No. 1; *J.*, 1917, 1140.
[9] *Bull. Imp. Inst.*, 1916, **14**, 565; *J.*, 1917, 604.
[10] L. E. Campbell, *Bull. Dept. Agric., Ceylon*, 1916, 24; *J.*, 1917, 92.
[11] L. E. Campbell, *J.*, 1917, 274-5.

From a German source[15] we are given the yields of so-called rubber from latex producing plants in Central Europe. The *Lactuca viminea*, of the natural order *Compositæ*, is said to contain nearly ½% of "pure caoutchouc." The plant, however, yields something over 19% of extractable substances, so that only a very small proportion of the latex consists of material which can be described as caoutchouc; even then we must not enquire too closely into the quality of the caoutchouc.

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[12] *Comptes rendus*, 1917, **165**, 123–5; *J.*, 1917, 970.

[13] G. M. Thomas and M. D. Maude, Eng. Pat., 104323, 1916; *J.*, 1917, 465.

[14] *Archief voor de Rubbercultuur*. *See J.*, 1917, 604.

[15] *Gummi-Zeit.*, 1916, **30**, 499–510; *J.*, 1917, 727.

The ordinary milkweed or spurge is said to yield less, 0·27 ; and the sow thistle (*Sonchus oleraceus*), 0·16 . To make these figures appear in a favourable light it is stated that *Hevea brasiliensis* and other rubber-yielding trees contain only 0·3 of rubber. Without enquiring how this calculation is arrived at, it may quite well be correct. Even the bark, when stripped off the *Hevea brasiliensis* tree, yields only minute quantities of rubber. The high yields from rubber estates are obtained, not by extracting traces of rubber which may be present in the felled tree, but by tapping the tree—a totally different matter. In fact, by a single tapping a larger amount of rubber can be obtained from a *Hevea* rubber tree than if the whole of the bark were stripped off, macerated, and the rubber extracted. A reference may also be made to a paper by F. Dannerth on chicle and chewing gums.[16]

NON-CAOUTCHOUC CONSTITUENTS OF RUBBER LATEX

It will be remembered that Eaton and his collaborators have shown that by setting coagulated rubber aside for a few days loss of nitrogen takes place, but the resulting rubber cures much faster. Further experiments showed this to be probably due to the action of a micro-organism. The present writer has carried this matter a stage further, and shown that this extremely active nitrogenous constituent, which may be termed the natural accelerator of Para rubber, consists of an organic base or bases[17] precipitable with phosphotungstic acid. These bases can be extracted from the rubber or separated from the serum. Their action is found to be very much more powerful than that of the more complex proteins. It has not been shown whether the latter are wholly replaceable by the bases. A further paper has appeared by Eaton and Day,[18] who have studied the distribution of nitrogen in the coagulum and serum of *Hevea* latex. The latter lost nitrogen very slowly, but the unrolled coagulum lost up to ¾ , calculated on the dry rubber, in six weeks.

In 1916 there appeared a large volume of researches on rubber carried out at the Delft Laboratories, entitled "Communications of the Government Institute for the Rubber Trade and Industry."[19] This has now become available to some extent to English students through the publication of a condensed version in English. Four parts have so far appeared, which deal with the composition of raw rubber and the viscosity of the solution. Some of the more interesting points in these papers may be referred to.

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[16] *J. Ind. Eng. Chem.*, 1917, **9**, 679; *J.*, 1917, 971.

[17] H. P. Stevens, *The Natural Accelerator of Para Rubber*; *J.*, 1917, 365–370.

[18] *Agric. Bull. F.M.S.*, 1916, **4**, 350–3; *J.*, 1916, 1164.

[19] Mededeelingen van den Rijksvoorlichtingsdienst ten behoeve van den Rubberhandel en de Rubbernijverheid, Dec., 1916.

P. Dekker[20] carried out dialysing experiments with latex preserved with ammonia. This latex gave 29% of caoutchouc coagulated by acid and 32·4% of total solids, leaving a difference of 3·4% soluble latex substances. On dialysis actually some 3·2% of soluble latex substances was removed, and a small quantity of nitrogenous matter (not ammonia) was found in the dialysate, confirming observations of Beadle and Stevens.[21] Having regard to the presence of organic bases in raw rubber, it would appear probable that these are responsible for a part at least of the nitrogenous matter in the dialysate. The solubility of a small part of the nitrogenous matter in acetone and water[22] when the rubber is extracted with these solvents, points in the same direction, as also the fact that the water extract contains nitrogen. This, however, is partly accounted for by the presence of other protein degradation products. An aqueous extract of rubber contains both organic bases and nitrogenous substances precipitable by tannin.[17] As regards the insoluble nitrogenous constituent, Dekker has separated this from various specimens of *Hevea* rubber by heating with petroleum[23] at 230°–260° C. for two to three hours. The whole of the ash of the original sample is contained in the insoluble part thus separated, but only about 55–65% of the nitrogen. The insoluble constituent separated by heating with petroleum contained 10·5% nitrogen in the case of plantation *Hevea* sheet and 7·3% in that of fine hard Para. These results may be compared with the earlier work of Spence and Kratz,[24] who isolated the insoluble constituent by swelling in benzine containing 0·3–0·5 trichloroacetic acid; this yielded the insoluble constituent containing on an average 9·83 to 12·08 of nitrogen in the case of plantation *Hevea*, and 7·75 to 10·5 for fine hard Para. It therefore appears that both methods yield similar figures as regards the nitrogen content of the insoluble constituent, but that the older figures of Spence and Kratz are on the whole higher. This leads to the conclusion that their method results in a more complete separation than that of Dekker. Dekker has also found[25] that the percentage of the insoluble constituent, as estimated by his petroleum method, is increased when the rubber is subjected to a preliminary heating, say for three hours at 130° C. Further heating for a longer period tends to reduce the percentage. The percentage of protein (nitrogen) in the insoluble constituent is correspondingly reduced, so that the increase noted appears to result from a decreased solubility of the caoutchouc.[26] This effect of heating is not brought about by oxidation, for a similar increase in the insoluble part takes place on heating in an atmosphere of carbon dioxide. A sample of rubber which normally yielded only 0·40 of insoluble matter gave 9·10 on heating in air for three hours at 130° C. and 20·25 on heating in carbon dioxide under the same conditions.

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[20] *Int. Assn. for Rubber Cultivation in Netherlands Indies*, Part 1, p. 23; *J.*, 1917, 970.

[21] *Koll. Zeits.*, 1913, **13**, 207.

[22] P. Dekker, *Int. Assn. for Rubber Cultivation in Netherlands Indies*, Part 2, 55 and 56. This observation is not new, the presence of nitrogen in the acetone extract having been noted by Spence and others.

[23] H. P. Stevens, "The Natural Accelerator of Para Rubber," *J.*, 1917, 365–370. Compare Beadle and Stevens, *Analyst*, 1912, **37**, 13; *J.*, 1912, 141.

VISCOSITY OF RUBBER SOLUTIONS.

A good deal of systematic work on this subject has been carried through at Delft[27] with the object of correlating the viscosity of rubber solutions with "the quality of the rubber either in the raw or vulcanised condition." Although the results do not record much progress in this direction they comprise some observations of interest to which reference will be made.

When determining the viscosity of a rubber solution in an ordinary Ostwald viscometer, it had previously been noted that the same solution tended to give lower results each time the determination was repeated. This effect was ascribed to a change in the solution brought about by the mechanical action of drawing the liquid through the capillary. Van Heurn[28] appears to have proved conclusively that this decrease in viscosity is not due to mechanical action, but to the action of light on the rubber solution during the operation. He has also shown that shaking the rubber and benzene together to promote solution is without effect on the viscosity of the solution obtained. Van Heurn has also repeated the fractional solution experiments of Stevens[29] and confirms the lower viscosity of the fraction first dissolved. It is therefore necessary, when making up solutions, to see that the rubber is dissolved as completely as possible.

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[25] *Int. Assn. for Rubber Cultn. in Nether. Indies*, Part 2, 63; *J.*, 1917, 1105.

[26] The increased insolubility on heating was originally noted by Gladstone and Hibbert, *J. Chem. Soc.*, 1888, 769.

[27] *Int. Assn. for Rubber Cultn. in Nether. Indies*, Part 3, 73–101 and Part 4, 111–120; *J.*, 1917, 1104, 1242.

[28] *Int. Assn. for Rubber Cultn. in Nether. Indies*, Part 3, 86–88; see *J.*, 1917, 1104.

[29] *India Rubber J.*, 1913, **46**, 345.

A few experiments of Van Heurn[30] indicate a rough proportionality between the viscosity and the breaking load of the raw rubber as influenced by heating and mastication. On the other hand, there is no direct proportionality in the case of vulcanised rubber, although it is claimed that a high viscosity points to a high coefficient of vulcanisation. This is somewhat surprising, having regard to the fact that the coefficient of vulcanisation is largely influenced by the presence of minute quantities of a catalyst (organic putrefaction base). Viscosity of a rubber solution is, according to the Dutch chemists, a measure of the degree of polymerisation, and the subject is discussed from this standpoint.[31]

Reference may also be made to the method of registering the viscosity. It is usual to determine the relative viscosity for at least three concentrations, and to plot a curve from the figures. Schidrowitz and Goldsbrough[32] take the tangent of the curve at a concentration of 1% as a measure of the viscosity, while Fol proposes to take the area bounded by the curve and both the axes. It is shown that the tangential method is unsatisfactory owing to the difficulty of drawing the tangents, different observers arriving at widely varying figures based on the same curve. Fol finds that a number of standard curves can be constructed so that one determination of the relative viscosity at an arbitrary concentration is sufficient to place the sample under investigation in its correct position relative to the nearest standard curve. This enables the so-called "viscosity number" to be calculated.

The Theory of Vulcanisation and the State of Cure.

It is well known that the state of cure or degree of vulcanisation has a great influence upon the physical properties of the rubber. With a short cure or a relatively low temperature, the rubber shows a high limit of elasticity and low tensile properties. As the length of cure or the temperature is raised, the limit of elasticity falls, and the tensile strength increases up to a certain point, after which it falls off and the rubber becomes brittle. It is consequently of great importance, when comparing rubbers for tensile strength and other physical properties, to ensure that all samples are vulcanised to the same degree or the same state of cure. The state of cure may be determined by the measurement of:—(1) The coefficient of vulcanisation which is based on chemical analysis of the vulcanised rubber. (2) The stress-strain curve, which is a measurement of the physical condition of the rubber.

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[30] *Int. Assn. for Rubber Cultn.*, Part 3, 98–100.

[31] *Int. Assn. for Rubber Cultn.*, Part 4, 111–121.

[32] *Koll. Zeits.*, 1913, **12**, 131 and **13**, 46.

Various workers in this sphere have found it necessary to fix on an ideal state of vulcanisation as a standard to which other states of vulcanisation can be referred. This is known as the optimum, perfect, or correct cure.

The coefficient of vulcanisation, which is the amount of "combined sulphur" (that which cannot be extracted with acetone) calculated on the rubber, was exhaustively investigated by D. Spence, who recently stated[33] that "the combined sulphur at optimum cure in the case of *Hevea* plantation rubber is a remarkably constant quantity, equal on the average to approximately 2·8–3 %." Also, the writer has said[34] that "a figure for the coefficient exceeding 3·5 in the case of a vulcanised rubber and sulphur compound is an almost certain indication of over-curing."

On the other hand, basing their results on the stress-strain curves, Schidrowitz and Goldsbrough,[35] working with a mixing of plantation rubber with 8 % of sulphur, obtained figures varying from 2·03 to 4·86 for the percentage of combined sulphur for samples subjected to the "correct cure" as ascertained by their method of physical testing.[36] It will be noted that a figure of 4·86 for combined sulphur corresponds to a coefficient of a little over 5. These authors found the optimum cure to vary from 1¾–4 hours at a temperature of 141° C. Also O. de Vries,[37] working with a mixing of rubber with 7½ % of sulphur, obtained figures from 4–5 for the percentage of combined sulphur for correctly cured rubber. This corresponds to a state of cure at which the specimen gives the maximum tensile strength. De Vries[38] finds the optimum cure usually requires 2–2¼ hours at a temperature of 148° C. Eaton and Day,[39] working with a mixing of 90 % of rubber and 10 % of sulphur, state that the limits for the sulphur content of rubber at the optimum cure vary between 3·7 and 4·8 %. Ordinary crêpe gives figures falling between 3·7 and 4·1 %, and "slab" between 4·2 and 4·6 %. The optimum cure for ordinary crêpe is about three hours at a temperature of 140° C.

It therefore appears that, according to de Vries and Eaton and Day, the combined sulphur or coefficient at the optimum cure varies for typical plantation rubbers within moderate limits, the minimum being about 25 less than the maximum. On the other hand, Schidrowitz by his method obtains a much wider variation. He emphasises the fact that he does not draw final conclusions from these results but is of opinion that so far they suggest that the combined sulphur at the optimum cure is not approximately constant.

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[33] *India Rubber J.*, 1916, **52**, 861; *J.*, 1917, 92.

[34] *J.*, 1916, **35**, 874, also *India Rubber J.*, Feb. 10, 1917.

[35] *India Rubber J.*, 1916, **52**, 505; *J.*, 1916, 550.

[36] See *Annual Report*, Vol. I, p. 210.

[37] *Mededeelingen van het Centraal Rubberstation*, No. 1, p. 5.

[38] *India Rubber J.*, 1917, **53**, 18.

[39] *J.*, 1917, **36**, 16–20 and 1116–1119.

Spence[10] originally showed that vulcanisation as determined by an increase in the combined sulphur proceeds extremely slowly at temperatures below 80° C., so that months are required to produce an appreciable increase in the combined sulphur. De Vries found that, keeping vulcanised specimens having a low coefficient (2·85) in an oven at 70° C. for 66 hours, the tensile properties were so altered that the rubber resembled one vulcanised ordinarily to give a coefficient of 4·5, that is to say, one given the optimum cure from de Vries' standpoint. This alteration in the tensile properties took place without any change in the coefficient. He therefore concluded that "the percentage of combined sulphur is quite independent of the state of cure as expressed by the position of the stress-strain curve." No objection can be taken to this statement if one admits that the "state of cure" is correctly expressed by the stress-strain curve. This, however, raises the whole question as to whether the state of cure is not more correctly expressed by the coefficient of vulcanisation. The results obtained both by de Vries and by Eaton and Day show that, when the physical tests are made under the same conditions, the coefficient roughly corresponds with the stress-strain curves. Eaton, who holds that the coefficient of vulcanisation and the stress-strain curves should correspond closely, points out that de Vries, by his treatment, is able to produce samples "containing almost any percentage of combined sulphur up to but not exceeding the normal figure obtained by direct cure." The results obtained by de Vries are therefore really due to an "accelerated 'ageing period.'" The importance of the "ageing" factor was originally emphasised by the writer[11] in a series of vulcanisations at the same temperature, but for increasingly long periods; the samples were allowed to age at room temperatures, and tests repeated at intervals. The results of such tests on typical pale crêpe and smoked sheet rubber showed that appreciable deterioration (as indicated by the tensile figures) sets in with both types within a twelvemonth in those cases in which the coefficient exceeds approximately 3·5. No appreciable deterioration was shown in the samples vulcanised having a coefficient of 3·2. These results lead to the conclusion that the period elapsing between vulcanising and testing should be constant, and from the experiments of Spence referred to above it also follows that the temperature should also be kept constant during this period.

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[10] *Koll. Zeits.*, 1912, **10**, 299; *J.*, 1912, 651.

[11] *J.*, 1916, 872–4.

There does not seem to be much doubt that the coefficient and tensile properties do not necessarily go hand in hand and that a considerable variation in the tensile properties may be effected without alteration in the coefficient. This was shown to be the case in a careful series of ageing experiments made by Spence as long ago as 1912,[42] and which appear to have been overlooked by recent workers. It was shown that very small increases in the coefficient could be detected in vulcanised rubber kept at ordinary temperatures over a period of three months, particularly in the fully cured or over-cured specimens. He also showed that excessive mastication previous to mixing had no influence on the coefficient, but a marked effect on the tensile properties.

It is open to question whether it is possible to vulcanise rubber so that it will maintain its physical properties unimpaired over a long period. A progressive reduction in the elongation under a given load appears to take place with ageing;[43] that is to say, the stress-strain curves tend to come lower down on the paper, the effect being similar to a longer cure or a higher temperature.[44] This can be seen from de Vries' results in the difference between the same sample tested two hours and 24 hours after vulcanisation.

From various published papers it appears that there is no standard state of cure in manufacturing practice. When adjusting the conditions of vulcanisation (time, heat, percentage of sulphur, accelerators, etc.), the manufacturer has in mind the ultimate purpose for which the goods are required. If high tensile strength is of less importance than flexibility and ageing qualities, the coefficient is kept low, particularly in cases where the goods are exposed to a relatively high temperature during use, as, for instance, the inner tube of a motor tyre. In such a case the conditions are similar to those of the ageing experiments already referred to. In other cases, where high tensile qualities are of first importance, the rubber is more "fully" cured. There is, therefore, in practice no one optimum cure, but rather an optimum cure for each individual article. Generally speaking, the optimum cure is that giving the maximum physical properties consistent with a reasonable life, having regard to the purpose for which the goods are required.[45]

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[42] *Koll. Zeits.*, 1912, **10**, 299; 1913, **13**, 265; *J.*, 1912, 651; 1913, 1120.

[43] H. P. Stevens, *J.*, 1916, 873.

[44] O. de Vries, *India Rubber J.*, 1917, **53**, 101; *J.*, 1917, 296.

The mixing commonly used by investigators when comparing the qualities of raw rubber contains 7½–10% of sulphur without other ingredients. Rubber thread is a type of manufactured rubber which resembles such a mixing most closely, and it is therefore of interest to note the results of analyses of this material recently published by Dubosc.[46] The ash found amounted to about 2% only, showing absence of loading. The acetone and alcoholic potash extracts were low or negligible. In the seven samples examined, the total sulphur varied from 2·68% to 3·04%. The figure for total sulphur will only slightly exceed that for combined sulphur, as it is usual for the manufacturer to digest the vulcanised thread in a hot alkaline solution after vulcanisation, which removes most of the free sulphur and prevents blooming of the finished goods. We may therefore conclude that the combined sulphur in these samples was under 3%.

The whole matter is closely bound up with the theory of vulcanisation. As in the cognate industries of tanning and dyeing, there are rival theories as to the chemical or physical nature of vulcanisation. It is, however, admitted by those who interpret the process as a chemical reaction that it may be preceded by a physical change, namely, a preliminary adsorption of the sulphur by the rubber, while the physicists admit that the absorption may be followed by a chemical reaction. The two schools differ as to whether the change which rubber undergoes in the process of vulcanisation is *primarily* of a chemical or physical nature. The latter view was originally championed by Wo Ostwald,[47] but the exhaustive quantitative researches of Spence and his collaborators[48] showed that most of the experimental work on which the physicists based their adsorption theory was unreliable, and proved that:

(1) The rate of combination of rubber and sulphur is mainly[49] proportional to the time of heating (vulcanising).

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[45] Various papers in the *India Rubber J.*, 1917, by Schidrowitz and Goldsbrough, de Vries, and Stevens; see *J.*, 1917, 296, 396, 971.

[46] *Caoutchouc et Gutta Percha*, 1916, **13**, 9007-8; *J.*, 1916, 1027.

[47] Wo Ostwald, *Koll. Zeits.*, 1912, **11**, 34.

[48] *Koll. Zeits.*, 1911, **8**, 304, **9**, 300; 1912, **10**, 28; *J.*, 1911, 817; 1912, **31**, 785.

[49] Eaton and Day, *J.*, 1917, **36**, 19, show three curves similar to Spence's but not so regular. Spence's curves are straight lines so long as 10% of the sulphur remains uncombined, while Eaton and Day's show slight curvature throughout. I

(2) For a mixing of rubber with 10% of sulphur, a velocity coefficient of 2·65 is obtained (since confirmed by de Vries[50] and others)

(3) Vulcanising with a large excess of sulphur (37%) compounds are formed with increasing quantities of combined sulphur up to 31·9%, after which further heating has no effect ($C_{10}H_{16}S_2$ contains 32% of sulphur).

(4) Bromination of rubber yields a definite tetrabromide, $C_{10}H_{16}Br_4$, but if a vulcanised rubber be brominated, less bromine combines, the deficiency of bromine being equivalent to the sulphur present in the rubber as combined sulphur

More recently a paper on the theory of vulcanisation has been published by Harries on work carried out in conjunction with Fonrobert.[51] A mixing of Para rubber and 10% of sulphur was vulcanised for a relatively short period (30 minutes at 145° C.), and exhaustively extracted with acetone over a period of 60 days; progressive reduction in the sulphur content took place, the final products containing only 0·29%. This amount is regarded by the authors as negligible, and it is concluded that vulcanisation can take place without chemical combination between the rubber and sulphur. Consequently, vulcanisation is primarily a physical and not a chemical phenomenon. Harries, however, distinguishes between this type of vulcanisation and "after-vulcanisation" in the course of which 2·4% of sulphur enters into combination. This view, however, would not appear to be reconcilable with the results of Spence and de Vries already referred to, in which it was shown that "after-vulcanisation" at temperatures below 80° C., which involves a considerable change in physical properties, is accompanied by a trivial increase in the combined sulphur. The main properties of raw and vulcanised rubber relied on by Harries as distinguishing characteristics, appear to be the insolubility of the latter in organic solvents and the greater resistance

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suggest this may be due to the fact that Spence used an acetone-extracted rubber (*i.e.* partly deprived of accelerator), while Eaton and Day used ordinary sheet and crepe which would contain the usual proportion of natural accelerator The slab sample (244A, see Eaton and Day's Paper) will contain the largest proportion of natural accelerator and gives a more pronounced curve than the sheet rubber (244B), while the crêpe rubber (244C), which would contain the smallest proportion of natural accelerator, approaches most closely to a straight line

[50] O. de Vries, *Mededeelingen van het Centraal Rubberstation* (1), p 31; see *J.*, 1916, 1226

[51] Harries, *Ber*, 1916, **49**, 1196 Harries and Fonrobert, *Ber*, 1916, **49**, 1390 *J.*, 1916, 747, 1027.

to reagents such as ozone. He therefore regards the vulcanised rubber as the stable and the raw rubber as the metastable form. This work appears to have been undertaken as a preliminary to future work on the regeneration of vulcanised rubber. If vulcanisation is primarily a physical phenomenon, the removal of the combined sulphur (desulphurisation) is only of secondary importance. It is worth noting that the various "reclaiming" processes at present in use do not so much aim at devulcanisation as the regeneration of the physical properties possessed by the compounded rubber previous to vulcanisation that is to say, plasticity, evenness of texture (homogeneity), and the capacity (when again subjected to the vulcanising process) to harden and toughen, the mass formed resembling the original vulcanised product. In this aim, modern reclaiming processes are more or less successful, particularly when it is remembered that the raw material the rubber waste often contains but a small proportion of vulcanised caoutchouc and that, perhaps in a "perished" or semi-decomposed state. A reclaiming process for the removal of the combined sulphur from vulcanised rubber has been recently patented by D. Spence.[52] Various claims had previously been made to the same end, but the only work of this nature that need be considered here is that of Hinrichsen and Kindscher,[53] who employed alcoholic soda and metallic powders. Their claim is disputed by P. Alexander.[54] Another process which is claimed to desulphurise vulcanised rubber has been patented by W. Esch,[55] who, after removing the "free" sulphur, treats the rubber in a phenolic solvent with an alkaline solution and heats the emulsion thus formed with zinc or aluminium. The emulsion is then treated with carbon dioxide, and, after settling, the solution of "depolymerised" rubber is removed. The solvent is recovered by steam distillation, and the recovered rubber "polymerised" by treating with 5 of sodium. The use of sodium for the improvement of low-grade rubbers was discovered and patented some years ago by Spence. It is well known that even prolonged treatment with solutions of caustic alkalis removes nothing but free sulphur; the combined sulphur is not affected. Spence's process[52] starts with a preliminary treatment to remove the free sulphur. The product obtained is dissolved by heating with a suitable solvent such as xylol, and this is then treated with an agent capable of combining with the sulphur, such as finely divided anhydrous caustic alkali, the reaction taking place in the presence of a vulcanising accelerator. The novelty of the process consists first in the use of dry reagents, and secondly in the use of a vulcanising accelerator which in the circumstances promotes devulcanisation in the same way as it promotes vulcanisation in the absence of soda, that is, under ordinary vulcanising conditions. As caustic soda itself is an accelerator, it follows that the desulphurising agent may act as its own accelerator. In this manner the amount of combined sulphur was reduced from 4·4 to 1·2. By the use of a solution of metallic sodium in aniline the combined sulphur was reduced to 0·9, and a hard rubber containing 32 combined sulphur reduced to 8·9. It is interesting to note that the desulphurised rubbers, including that containing 8·9 of combined sulphur, were soluble in benzene.

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[52] U.S. Pat. 1235852, 1917; *J.*, 1917, 1056.

[53] Hinrichsen and Kindscher, *Mitt. K. Materialpruf.*, 1915, **33**, 407 415; *J.*, 1916, 934.

[54] *Koll. Zeits.*, 1912, **10**, 252.

[55] Ger. Pat. 293496, 1912; *J.*, 1916, 1071.

ACCELERATORS

The use of accelerators appears to be widening. Manufacturers of rubber-compounding ingredients, as well as rubber manufacturers themselves have been granted licences for working the Bayer patents, and accelerators under trade names have appeared on the market. D. Spence[56] claims to have anticipated the Bayer patent for piperidine and also that of S. J. Peachey for *p*-nitrosodimethylaniline; this has called forth a vigorous reply from the latter.[57] Finally, the use of caustic alkalis in glycerin or other suitable solvent, has been patented by the Dunlop Rubber Co. and Twiss.[58] The accelerating effect of basic mineral substances is well known, but the general idea previously prevailing regarded alkalis as dangerous and the goods liable to "perishing" and decomposition. Twiss states, however, that his samples did not show a greater loss in strength than those vulcanised in the ordinary manner. A reference was made to Martin's work on this subject in the last Report (p. 207). Even lime has been regarded as open to suspicion, magnesia coming more into use.

Reference may here be made to the vulcanising tests made by Gottlob[59] with an organic accelerator. An increase in rate of vulcanisation amounting to 200–300, was shown by the percentage of combined sulphur on a rubber and sulphur mixing containing 10 of sulphur. The most interesting part of the paper deals with ageing tests on the vulcanised samples, and it is shown that the tendency to "perishing" and decomposition of the fully or over-vulcanised specimens was much greater in those samples cured with the use of an accelerator than those without.

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[56] *J.*, 1917, 118-119.

[57] *J.*, 1917, 321.

[58] Eng. Pat. 110059, 1916; *J.*, 1917, 1185.

[59] *Gummi-Zeit.*, 1916, **30**, 307.

VULCANISATION.

The condition of the sulphur used for vulcanisation has been investigated by Twiss,[60] who compared the effect produced by the soluble and insoluble varieties. There is much *a priori* evidence in favour of such a theory, which is set out at length by Twiss in his paper. Two mixings were made of rubber with 10% of sulphur, one with soluble and the other with the insoluble variety, and it was found that the former combined slightly faster with the rubber than the latter; the "free" sulphur extracted with acetone from the rubber vulcanised with the insoluble variety of sulphur consisted mainly of the soluble modification. Twiss also draws attention to the difficulty of extracting the insoluble modification with acetone, only some 27% being extracted in 10 hours from the unvulcanised compound containing this modification. Dubosc[61] has formulated a theory of vulcanisation according to which the sulphur at the moment of reaction must be in the colloidal form. This is produced *in situ* by a reaction between hydrogen sulphide and sulphur dioxide, the former derived from the action of the sulphur added with the resins, protein, etc.

A reference may also be made to the writer's further work on the influence of the resinous constituents on the vulcanising of rubber.[62] The effect produced by extraction of the raw rubber with alcohol or acetone is much more pronounced in mixings containing litharge. A reduction in rate of cure is observed even in the case of rubber and sulphur mixings, and is no doubt due to the extraction of the natural accelerator with the resinous matter. As regards vulcanisation with nitro-aromatic derivatives and organic peroxides, it would appear that so far the results obtained are not comparable with a fully vulcanised rubber manufactured with sulphur as the vulcanising agent.[63]

A very complete account of the present position of the chemistry of vulcanisation is given by D. F. Twiss in a paper read at the Annual Meeting (1917) of the Society,[64] and reference may also be made to a paper on the present position of synthetic caoutchouc by B. W. D. Luff.[65]

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[60] *J.*, 1917, 788.

[61] *Caoutchouc et Guttapercha*, 1917, **14**, 9109-15; *J.*, 1917, 296.

[62] *J.*, 1916, 874-7.

[63] H. P. Stevens, *J.*, 1917, 107-9.

[64] *J.*, 1917, 789.

[65] *J.*, 1916, 983-9.

LEATHER

By JOSEPH T. WOOD, F.I.C.

Messrs. Turner, Bros., Ltd., Nottingham

IN the tanning industries the quantity of work, both in research and investigation of processes, continues to suffer from the war.

The younger men in the two British centres—London and Leeds, are serving in the army, and the chemists who have remained behind in the works and laboratories have had their attention confined principally to problems connected with the rapid production of leather for army use, and have had neither time nor inclination to read papers or publish new work.

The principals have been consulted by the War Department, and have rendered valuable aid by their advice in technical matters. The results achieved have surpassed expectation, and both the British Army, and many of the Allied troops, have been supplied with boots and equipment of better quality than in any previous war.

Mention should also be made of the vast quantities of sheep leather which have been turned out for jerkins for the winter, and for aviators' clothing and gloves.

PREPARATORY PROCESSES

Preservation and disinfection of hides and skins. Joint regulations[1] have been drawn up by the Secretary of Agriculture and the Secretary of the United States, governing the certification and disinfection of hides, fleshings, hide cuttings, &c., for entry into the United States. The circular of the Treasury Department (T. D. 36, 751)[2] contains these regulations, which took effect on January 1st, 1917.

A. Seymour-Jones[3] continues his work on the sterilisation and curing of dried hides, especially with reference to anthrax. He states that the Schattenfroh process of sterilisation (see Annual Report, Vol. I., p. 227) damages the fibres of the skin, and moreover would not be practicable in the hands of ignorant natives. The efficiency of the formic-mercury process has been proved in practice, and it is suggested that the Governments concerned should forbid the importation of hides and skins unless (1) they have been submitted to the ordinary "wet-salting" process immediately after flaying; or (2) if cured by drying they have been converted back to the "wet-salted" state by the formic-mercury process before leaving the country of export.

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[1] *J.*, 1917, 39.

[2] Reprinted in the *Board of Trade Journal*, Dec. 21, 1916, pp. 884-887.

[3] *J. A. L. C. A.*, 1917, 68; *Coll.* (London), 1917, 121.

A. Eichhorn, W. N. Berg, and R. A. Kelser[4] publish immunity studies on anthrax serum, and give results of methods for its examinations, and also the results of experiments on animals. In many cases death was prevented.

The meeting of the A.L.C.A. in June, 1917,[5] at Atlantic City, was devoted to the discussion of anthrax. The following papers were read:—"Anthrax," A. S. Ross; "Practice and Theory of Treatment and Diagnosis of Anthrax," H. J. Frisbie; "The Nature of Anthrax and Anti-Anthrax Serum," A. Parker Hitchens; "Anthrax and Hide Disinfection," Van A. Wallin; "Discussion on Anthrax," R. W. Hickman and others.

The practice of bringing together a number of experts on the same subject is an excellent one, and brings to light matters which otherwise would remain hidden from the general public. Our own societies might take pattern by it.

Useful directions for the treatment of anthrax are given by C. B. Oberfell.[6]

At the same meeting A. Seymour-Jones read a paper on the future of hide supply, pressing for the improved preservation of hides imported from foreign countries. There is no doubt that skins preserved as he suggests (by the formic-mercury process) would be better for the tanner, and the risk of infection by anthrax would be avoided. It does not appear that much can be done until the Governments of the chief importing countries come to an agreement on the matter, and make the system of preservation compulsory.

A paper by R. M. Chapin[7] on the chemical composition of lime-sulphur animal dips, is of interest to leather manufacturers on account of the explanation given of the reactions which take place in the preparation of lime-sulphur solutions used in unhairing.

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[4] *J. Agric. Res.*, 1917, **8**, 37; *J.*, 1917, 302.

[5] *J. A. L. C. A.*, August, 1917.

[6] *J. A. L. C. A.*, 1917, 51.

[7] *U.S. Dept. Agric. Bull.* No. 451, 1916; *J.*, 1917, 232.

Puering and bating. J. Meister[8] patents the use of pepsin for the deliming and bating of skins. These are submitted to the action of pepsin in very dilute hydrochloric acid, the temperature being maintained at 40° C., and other acids (boric, lactic) and also salts (ammonium chloride) are added to keep up the hydrogen concentration. In view of the fact that pepsin acts in acid solution of a concentration equal to 0·2% hydrochloric acid, it is quite certain that the skins would be swollen to such an extent as to render them useless for tanning.

A new antiseptic, "mercurophen" (sodium oxymercuri-*o*-nitrophenoxide) is described by J. F. Schamberg, J. A. Kolmer and G. W. Raiziss.[9] By the Rideal-Walker test it exhibits 10,000 times greater germicidal power than phenol, against *B. typhosus*, and over 30 times greater activity than mercuric chloride. It is suggested by a writer in the *Leather World* that this antiseptic might be of use for the disinfection of hides and skins in a similar way to the use of mercuric chloride in the Seymour-Jones formic-mercury process.

Pickling. Restrictions in the supply of sulphuric acid have led to the trial of nitre cake as a substitute for acid in the pickling process. The cake contains from 26 to 30% of sulphuric acid, and a solution to which is added the proper quantity of common salt may be used for pickling. The storing and solution of the cake present some difficulties, and its use requires control from the laboratory.[10]

E. Nihoul[11] gives an account of the commercial manufacture of lactic and butyric acids, together with methods of analysis. There is no doubt that after the war the use of these acids in the various preparatory processes will be largely increased.

TANNING.

Vegetable tannage. N. Flamel[12] gives a useful general review of the various processes proposed from 1761 to the present time for lessening the time of tannage in the production of leather. The general conclusion arrived at is that leather rapidly tanned, by means of vegetable tanning materials, is not equal in quality to leather tanned by the slow process. Rapidly tanned leathers in general contain a larger percentage of water-soluble material than those more slowly tanned, although this difference is not distinctive.

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[8] Fr. Pat. 480196, 1915; *J.*, 1917, 151.

[9] *J. Amer. Med. Assoc.*, 1917, 1458; *J.*, 1917, 733.

[10] For a discussion on the subject, and references to previous papers, see *J.*, 1917, 1216.

[11] "A propos des acides lactiques et butyriques." *Coll.* (London), 1916, 242.

[12] *Rev. Gén. des Sciences*, 1916, 720; *J. A. L. C. A.*, 1917, 142.

A valuable paper on drum tannage, containing many practical wrinkles, by Oskar Riethof,[13] includes a table showing the degree of tannage and per cent. of hide substance in different standard tannages. When properly controlled the tensile strength of drum or tumbler tanned leather is fully equal to that of pit tanned leather. Procter also has shown that a very high percentage of combined tannin (degree of tannage) actually reduces the breaking resistance.

F. A. Coombs[14] gives an account of comparative sole leather tests with Australian pine barks (see Ann. Rep., vol. I, 1916, p. 240), and a comparison of these with wattle barks. These experiments were carried out on one hide, the butt of which was cut into eight pieces, a diagram of the method of cutting the hide being given. The results show a higher leather return for the pine bark tannage, probably due to the higher acidity of the pine liquors. The leather also resisted water penetration better than the wattle bark leather. The author suggests the drawing up of a standard experimental process for tanning heavy leathers based on these trials. He considers that such a process must be a miniature reproduction of the commercial process.

F. A. Coombs, F. Alcock, and A. Stelling[15] have also given some useful comparative tests on similar lines with mangrove and wattle barks.

Riethof[16] publishes a series of useful tables showing the relation between specific gravity, per cent. total solids, and tannins in chestnut extracts and hemlock bark extracts.

M. C. Lamb[17] discusses the causes of the deterioration of leather used in gas meters, and gives specifications for the manufacture of suitable leathers for this work from E. I. Persians, semi-chrome tanned, and pure chrome tanned sheep or lambskins.

E. Nihoul[18] gives a list of eight different tanning materials found in the Belgian Congo. The tannin content varies from 12 to 28 %; he considers that some of these could be economically used in Europe especially if dry extracts of them were made in the Congo.

Other useful information with regard to vegetable tanning materials is given in the following papers:—

Quebracho Extract Manufacture in Argentina and Paraguay. Board of Trade J., February 15th, 1917. J., 1917, 226.

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[13] *J. A. L. C. A.*, 1917, 322; *J.*, 1917, 932.

[14] *Coll.* (London), 1916, 205; *J.*, 1916, 1028.

[15] *J.*, 1917, 188.

[16] *Coll.* (London), 1915, 232.

[17] *Coll.* (London), 1916, 248; *J.*, 1916, 989.

[18] Note sur quelques matières tannantes du Congo Belge, possibilité de leur utilisation en vue de la fabrication d'extraits secs. *Coll.* (London), 1916, 257.

Tanning Materials from British Malaya, Chamber of Comm. J., March, 1917. J., 1917, 347.

Indian Sumac, Bull. Imp. Inst., 1916, **14**, 182; Coll. (Lond.), 1917, 2.

Indian Sumac. Puran Singh, Ind. Forest Bull. No. 31, 1916. J., 1917, 39.

The Wattle Bark Industry of Natal. Bull. Imp. Inst., **14**, No. 4, 599. J., 1917, 558.

"Tarwad" Bark as a Tanning Agent. D. B. Limaye, Coll. (Lond.), 1917, 126. (A very full account. This bark, *Cassia auriculata*, along with babul and myrabolams, form the chief tanning materials used in the tanning of East India kips.) J., 1917, 513.

Babul Pods as Tanning Material. Bull. Imp. Inst., 1916, **14**, 612. J., 1917, 559.

Indian Forest Products. R. S. Pearson. Lecture at the Soc. of Arts. J., 1917, 631.

Philippine Tanbarks. V. Q. Gana. Philipp. J. Sci., 1916, **11**, 231. J., 1917, 1106.

Liquors from the sulphite cellulose process of wood pulp manufacture are put on the market under various names such as "spruce extract," the tanning properties of which are doubtful, but which act as filling materials. In some cases they are used to adulterate genuine tanning extracts. The process of manufacture of wood-pulp is described in a paper by Allan Smith.[19]

The detection of wood-pulp in extracts and leather is dealt with by W. Appelius and R. Schmidt, Leder Tech. Rundschau, 1911, 29, Abstract in Coll. (Lond.) 1916, 288.

J. Paessler[20] has examined the tannin content of green walnut shells. They contain 22% of a tannin which, though sensitive, is usable. He recommends the collection of these shells for leather manufacture.

A. Seymour-Jones[21] outlines a process for the rapid tanning of sole leather. Instead of removing lime by the suspenders, it is either neutralised or removed by sodium hyposulphite. The hides are then immersed in a neat extract; the tanning will be completed in about 10 days to a fortnight, after which the hides should be laid away in a strong but diluted liquor. In this way the whole operation of tanning may be completed within three weeks.

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[19] *J.*, 1916, 281.

[20] *Ledertechn. Rundschau*, 1916, **8**, 189; *J.*, 1917, 605.

[21] *J. Soc. Leather Tr. Chem.*, 1917, 2.

Neradol.—Patents still continue to be taken out for tanning substances resembling neradol. The Deutsch-Koloniale Gerb- u. Farbstoff Ges.[22] patents the manufacture of tanning substances obtained by the action of formaldehyde, or a substance capable of yielding formaldehyde, on aminonaphtholsulphonic acids or dihydroxynaphthalenesulphonic acids as such, or in the form of their salts in aqueous or slightly acid solution.

The Society of Chemical Industry in Basle[23] patents the use of soluble aromatic compounds containing two or more sulphamino groups, together with a sulphonic group, but no hydroxyl or free amino groups. The leather produced is not coloured, and is very similar to vegetable tanned leather.

G. Calvert[24] patents a tanning agent obtained by the interaction of a phenolic substance and formaldehyde in the presence of soap. Since reaction is carried out in the cold it seems doubtful if substances of the type of neradol are formed, in which case the tannage would be a formaldehyde tannage.

Mineral tanning.—E. Nihoul[25] publishes a comprehensive review of the alum tannage, which is of both theoretical and practical value; although the use of alum in tawing is of very great antiquity, the theory of the process has not been studied so thoroughly as that of chrome tanning.

O. Röhm[26] patents a process for tanning with salts of iron in combination with tannin, a phenol, and an aromatic carboxylic acid. In a further patent[27] the salts of iron are applied in conjunction with formaldehyde. It certainly seems an anomaly that an enemy country is enabled to take out patents here which in many cases are merely "blocking" patents and have never been worked out on a practical scale. A number of patents of this description are being taken out for the application of synthetic products on the same lines as neradol.

P. Kauschke[28] patents a process for the preparation of chrome liquors containing complex organic chromium salts. Chromic acid is reduced in concentrated sulphuric acid solution by means of waste materials containing protein, waste chrome leather, scrap cuttings or parings, reaction being started either by heating or by adding dehydrating or easily oxidisable substances or substances capable of generating nascent hydrogen.

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[22] Eng. Pat. 18174, 1915; J., 1917, 93.

[23] Ger. Pat. 297187; J., 1917, 855.

[24] Eng. Pat. 108262, 1916; J., 1917, 1019.

[25] Coll. (London), 1916, 178; J., 1917, 69.

[26] Eng. Pat. 103295.

[27] Eng. Pat. 103827; J., 1918, 14A.

[28] Ger. Pat. 295518, 1914; J., 1917, 298.

M. C. Lamb and A. Harvey,[29] in a paper on the "Estimation of Chrome Oxide in Chrome Leather," state that a properly tanned chrome leather should contain a minimum of 3% Cr_2O_3. They also point out that the fat should be extracted from the leather before the analysis is made.

Oil tannages.—A. Chaston Chapman[30] publishes a very interesting and valuable research on the occurrence in certain fish oils of high percentages of hydrocarbons. In some fish oils very considerable quantities of unsaponifiable hydrocarbons, with very high iodine values, occur. Unless all the constants of such oils are determined, this might lead to the assumption that the oil was adulterated with a mineral oil. Chapman has given the name "spinacene" to this hitherto unknown hydrocarbon and gives full details of its properties. A point of great importance to the analyst is that it would appear to be difficult to express a definite opinion as to whether a given sample consists of shark liver oil or not.

Finishing processes.—M. C. Lamb and A. Harvey[31] have examined a large number of animal and vegetable products used in the finishing of leather, and suggest certain standards of quality for these products. Results are given for blood albumen, Irish moss, algin, gum tragacanth (*Astragalus gummifera*), gum acacia, gum tragasol and casein.

T. E. Durrant[32] gives an account of "grains" on leather useful for the identification of different skins in printed condition.

Sulphonated oils.—The use of these oils for fat-liquoring has further increased during the past year, but owing to the increasing scarcity of castor oil a variety of other oils have been used which in many cases have not given such good results as sulphonated castor oil. Further, increasing adulteration with mineral oils and ammonia soaps has caused tanners and finishers to pay more attention to the analysis of these oils. This has been the case especially in America, where very valuable work has been done by a committee of the A. L. C. A. under the chairmanship of W. K. Alsop.[33]

One of the points brought out is that there is no well recognized method of determining the source of the oil from which a sulphonated oil has been made If a mixture of oils be sulphonated, including an easily sulphonated oil, such as castor oil, and one more difficult to sulphonate, and then the neutral oils separated, and their constants determined, the presence of castor oil is not apparent, but that of the other oils is, and wrong conclusions would be drawn from such results. Alsop's report of the 1917 committee for the analysis of sulphonated oils should be in the hands of all chemists interested in this work.

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[29] *Coll.* (London), 1916, 201; *J.*, 1916, 1028.

[30] *Chem. Soc. Trans.*, 1917, **111**, 56; *Analyst*, 1917, **42**, 161; *J.*, 1917, 392, 602.

[31] *J. Soc. Dyers and Colourists*, 1917, **33**, 19; *J.*, 1917, 212.

[32] *Leather World*, Dec. 4, 1916; Jan. 11, 1917.

[33] *J. A. L. C. A.*, 1917, 266, 140.

R. Hart, in a paper on the analysis of sulphonated oils, reaches the following conclusions. - Turkey red oils and similar products are completely saponified by $N/2$ alcoholic sodium hydroxide. Alkali combined as soap can be determined by titrating its solution with acid in presence of methyl orange. It is feasible to calculate the combined SO_4 from the increase of acidity due to the splitting of the sulpho group Based on these fundamental points a rapid method has been developed whereby sulphonated oils can be analysed for fat, ammonia and caustic soda bound as soap, and for sulphuric anhydride in the form sulpho-ricinoleic acid

Quite recently L. G Radcliffe and S Medofski[34] have published work on the sulphonation of fixed oils, with special reference to the textile and leather industries This paper contains an account of the discovery and constitution of the "Turkey red oils," together with details of the experimental work carried out by the authors to determine the constants of the fatty acids resulting from the saponification of the sulphonated oils. Data are given of sesamé, cotton-seed, and olive oils, which appear to show that the most easily sulphonated oils are those containing olein or oleic acid, and that the products of the reaction after saponification contain lactones and hydroxy-acids. The tables given are too extensive to be quoted here. The whole paper is a very valuable contribution to the constitution of sulphonated oils.

R. Kobert and W. Greuel[35] state that indications of the strength and action of commercial Turkey-red oils ("Solvines") can be obtained from experiments with blood corpuscles. On the results of their work they propose a method for the biological valuation of these oils; among other things it is suggested that saponins could be used as substitutes for Turkey-red oil in the tanning industry.

O. Rohm[36] patents the use of castor oil sulphonated just sufficiently to remain soluble after neutralization.

[34] *J. Soc Dyers and Col*, 1918, **34**, 22; *J*, 1918, 157A.

[35] *Coll*, 1916, 261; *J*, 1917, 91.

[36] Eng Pat 103668, *J*, 1917, 1141

T. Sandland[37] patents a composition for finishing and dressing leather for furniture. It consists of three parts of each hard drying elastic varnish, methylated spirit, and petroleum, one part of boiled linseed oil, and six parts of benzine or benzol. Pigments may be added as desired. The composition may also be used for the renovation of old and worn leathers.

Waste products.—America still leads the way in the study of the economical disposal of tannery wastes and sewage. D. D. Jackson and A. M. Buswell[38] investigated the subject from the point of view of prevention of anthrax infection of cattle due to the presence of anthrax bacilli in the tannery effluent. In the course of their investigations they obtained valuable information on the value of various disinfectants, sulphur dioxide, calcium hypochlorite, and chlorine. In a discussion on the above paper it was stated that 50 parts of chlorine per 1,000,000 killed anthrax spores suspended in the general effluent of the tannery. Liquid chlorine was found to be much more efficient than bleaching powder. The amount of chlorine used was sufficient to combine with all the organic matters, so that no free chlorine was found in the effluent. H. B. Hommon[39] gives details of sewage disposal plants at a tannery of sole leather in Virginia, and at a harness leather tannery at Cincinnati, Ohio, and also particulars as to the disposal of the sludge. The following tables given in the paper are of general interest.

ANALYSES OF THE RAW AND TREATED WASTES AT THE TANNERY OF THE DEFORD LEATHER COMPANY, LURAY, VA.

Source	Susp. Solids	Organic and free Ammonia	Nitrites	Nitrates	Oxygen consumed 30′ at 96° C
Beam house	850				600
Hair wash	900	–			200
Spent tan liquor	1,100	–			13,000
Composite	1,200	70			900
Effluent set. tank	450	55			530
Effluent cinder filter	160	30	0.29	6.0	205
Effluent sand filter	30	25	0.17	23.0	55

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[37] Eng. Pat. 17702, 1915; *J.*, 1917, 93.

[38] *J. A. L. C. A.*, 1917, 56, 229; *J.*, 1917, 895, 931.

[39] *J. A. L. C. A.*, 1917, 307; *J.*, 1917, 931.

ANALYSES OF RAW AND TREATED WASTES AT THE HAFFNER BROS. TANNERY, CINCINNATI, OHIO.

Source	Susp. Solid	Nitrogen as			Oxygen consumed 30′ at 96° C.
		Organic and free Ammonia	Nitrites	Nitrate	
Beam house	1,140	100			800
Spent tan liquor	900	60			3,900
Composite	1,130	100			1,000
Effluent set. tank	380	75			700
Effluent cinder filter	120	30			360
Effluent sand filter	45	13	0.4	10	85

TABLE SHOWING THE NUMBER OF GALLONS OF WASTE DISCHARGE PER DAY AND PER HIDE FROM THE DIFFERENT SOURCES AT THE TWO TANNERIES.

Type of Waste	Dyford Leather Co., Luray, Va.		Haffner Bros., Cincinnati Ohio	
	Gallons		Gallons	
	Per Day	Per Hide	Per Day	Per Hide.
Beam house	65,500	240	52,700	316
Hair wash	23,500	85	Do not wash hair	
Spent tan	14,000	51	2,800	17
Total	103,000	376	55,500	333

E. Ardern[10] gives an account of experiments made for the River Committee of the Manchester Corporation on the activated sludg process of sewage purification, in which he shows that, contrary to th opinion formed as the result of earlier experiments when working wit a strong sludge sewage, the maintenance of the activity of the slud is not dependent on the stage to which nitrification is carried. would appear that the cost of dewatering and drying the sludge will b more than repaid by the value of the resultant dry sludge.

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[10] J., 1917, 65. See *Report*, 1916, 237.

A. Harvey[41] gives a concise account of the methods used for the analysis of tannery wastes for use as manures at the South Eastern Agricultural College, Wye.

A further paper on the treatment of tannery sewage by C. L. Peck[42] gives a summary of results obtained in May, 1917, by the Dorr method of sedimentation.

M. C. Lamb[43] has brought together various proposals and methods for the utilisation of condemned army boots. One of the proposals is to cut the leather into small pieces, which are then mixed with asphalt bitumen and limestone, and used for laying the surface of roads (patent by S. Brough of Handsworth, 1910). Such a road is more resilient and noiseless than the ordinary macadam road. The Roads Board are now interesting themselves in the matter, and it is probable that the process will be introduced into practice. From a chemical point of view, dry distillation of the leather is of greater interest and promises good commercial results. The following products were obtained from the dry distillation of one ton of condemned army boots (500 pairs), prices based on market values October, 1917: 560 lb. purified charcoal, value £10; 515 lb. ammonium sulphate, value £1 2s. 9d.; 67 lb. of grease, value £1 10s.; and 125 lb. metal, value [illegible]0s.: a total of £16 11s. 9d., which should leave a good margin of profit. Several other methods of utilising old boots are given in Lamb's paper.

Machinery.—Owing to control of all engineering work by the Ministry of Munitions it has been extremely difficult for engineers to turn out new machinery or to keep the trade supplied with its normal requirements. The Committee on "Trade after the War," of which Sir Henry Ledgard is chairman, have met the trade engineers, and are endeavouring to work out a scheme so that they may be able to produce all the machinery required for the leather trade in this country. It seems probable that this can be done by the firms producing tanners' machinery combining instead of competing amongst themselves.

ANALYTICAL METHODS AND CHEMISTRY.

There has been no striking advance in the chemistry of tannins, or in new analytical methods, since the last report was written, but a good deal of steady, useful work has been done on present methods.

D. McCandlish and J. A. Wilson[44] reply to the criticisms of H. G. Bennett on their method for the determination of alkaline sulphides in lime liquors. The problem of determining accurately the amount of sulphide in lime liquors has never been solved to the satisfaction of all concerned.

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[41] *Coll.* (London), 1916, 151.

[42] *J. A.L.C.A.*, 1917, 422.

[43] *J.*, 1917, 986.

[44] *J.A.L.C.A.*, 11, Dec., 1916; *Coll.* (London), 1917, 10; *J.*, 1917, 93.

Bennett[45] continues the discussion on McCandlish and Wilson's method (see Ann. Rep., 1916, I, 229). He points out that the stronger the limes are in sulphide, the weaker they are in lime, hence in such liquors the tendency of hydrogen sulphide to escape is greater.

For very small quantities of sulphides, the method of W. A. Drushel and E. M. Elston[46] is suitable. This is a colorimetric method based on the liberation of hydrogen sulphide, which is absorbed by lead acetate paper.

Levi and Orthmann[47] estimate the total sulphur in leather by precipitating as barium sulphate after the organic matter has been destroyed by boiling the leather with a mixture consisting of potassium bichromate 50 grms., water 150 c.c., and concentrated hydrochloric acid 50 c.c.

H. G. Bennett[48] gives details of methods employed by him for the analysis of limed pelt. In determining the total alkalinity, the hydroxides and sulphydrates of calcium and sodium, ammonia and organic bases, are extracted from the pelt by means of a 3% solution of boric acid, and are then titrated with standard acid, using methyl orange, which is unaffected by the boric acid and by hydrogen sulphide. Details of the mode of estimation of ammonia, sulphide, soda, lime, hide substance, and salt are given, for which the original paper must be consulted.

H. G. Bennett[49] has determined the amounts of nitrogen in keratin from various sources. No difference was found between the keratin from ox-hide of various colours, or of the two sexes, or at different seasons of the year. The mean percentage of nitrogen was 16·3%. Keratin from dog hair (white fox-terrier) contained 17·2% N; that from goat hair 16·7% N; from human hair, woman 16·1% N, man 16·1% N; from finger nails 16·4% N.

The American Leather Chemists' Association[50] have published their revised official methods for the analysis of vegetable materials containing tannin.

In a very useful review of developments in the analysis of tanning materials. H. G. Bennett[51] discusses the official method of tannin analysis from the point of view of an adsorption phenomenon, detannisation with hide powder, being a case of surface action, and subject to the ordinary adsorption law.

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[45] *J. S. L. T. C.*, 1917, 3.

[46] *Amer. J. Sci.*, 1916, **42**, 155; *J.*, 1916, 925.

[47] *J. A. L. C. A.*, 1916, **11**, 196; *J.*, 1916, 1071.

[48] *Coll.* (London), 1916, 125; *J.*, 1916, 645.

[49] *Coll.* (London), 1917, 101.

[50] *J. A. L. C. A.*, 1916, **11**, 546–570.

As a result of the discussion it is concluded that the hide powder process would be greatly improved in both concordance and accuracy by the adoption of the following modifications. Detannisation of infusions of only half the strength now used, i.e., of solutions containing 0·2 of tannin approximately instead of 0·4. Neutralisation of all acidity of hide powder before chroming, and the employment of the more basic salt $Cr_2Cl_5(OH)$ for chroming purposes, thus obtaining a constant acidity of the hide powder, mainly due to non-swelling acids. The standardisation of hide powders by the determination of relative specific surface, and the employment of a constant active surface in each analysis. The use of 5 grms. of hide powder of the type now in use instead of 6·5 grms. In general, to use that quantity of hide powder, which is approximately 10 greater than the minimum amount necessary to detannise a 0·45 solution of gallotannic acid.

As a further result of the discussion,[51] Bennett considers there is little hope of changing the adsorbent, since substances which have been proposed as a substitute, such as oxides of copper, aluminium, lead, and nickel, detannise by adsorption rather than by chemical action, so that the errors are much the same as with hide powder.

The testing of hide powder is dealt with in the report of the Hide Powder Committee.[52]

The question of the effect of hard waters on the tanning process has recently received renewed attention in America. It is well known that in laboratory extractions of tanning materials with hard water a sensible loss of tannin occurs. The subject was exhaustively treated by Nihoul and his collaborators in several important papers,[53] and his results have recently been confirmed by E. Schell,[54] who finds that the carbonates in the water are the chief cause of the loss. A committee of the A. L. C. A. have now issued their report,[55] giving the result of a series of comparative extractions with distilled water and with various hard waters, in which the conditions were designed so as to be approximately analogous to those prevailing in tannery practice. The general consensus of opinion by the individual members of the committee as to the conclusions to be drawn from the tabulated results indicates a serious doubt as to any destruction of tannin by hard water as used in practice. It was shown, however, that salt had a detrimental effect in the leaching, and that total solids have more effect than temporary hardness. This may well be, since at the temperatures used the carbon dioxide in the water will be given off and the carbonates precipitated. The colour of the infusions from the hard water was darker than from the distilled water, and colour tests on sheep skin were redder with hard water than with distilled water. In the discussion which followed the reading of the report Mr. Smart said that in a certain tannery it was found that 20% more bark was necessary to tan a given quantity of hides when the leaching was done with hard water than when soft river water was used. It would appear from this that there are still some unknown factors in the problem, which probably differ in each tannery.[56]

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[51] *Coll.* (London), 1917, 52, 84.

[52] *Coll.* (London), 1916, 155.

[53] *Bull. Assoc. Belge des Chim.* 1903, **17**, 101; 1904, **18**, 155, 22; see *J.*, 1901, 1005; 1904, 122, 1155.

[54] *La Halle aux Cuirs*, Aug. 1917; *J.*, 1917, 1213.

[55] *J. A. L. C. A.*, 1917, 360; *J.*, 1917, 1056.

The important question of the determination of free sulphuric acid in leather has received attention in America by a committee of the A. L. C. A.,[57] the members of which carried out a series of comparative trials with the Wuensch and Procter-Searle methods. The results indicate that the Wuensch method is unreliable and fails completely in the presence of magnesium sulphate, which has no effect on the Procter-Searle method; the latter, however, does not give reliable results in the presence of iron, aluminium, ammonium, and chromium salts.

A quick and reliable method for the detection of neradol in leather is needed. Unfortunately both neradol and sulphite cellulose give a precipitate with the aniline test (Pocket Book, p. 56). Most of the reactions which have been proposed for the detection of neradol in leather either are not sufficiently sensitive or are interfered with by the presence of other tanning materials. E. Seel and A. Sander[58] give the following method:

20 grms. of the leather cut into small pieces is boiled with 200 c.c. of water for 15/30 minutes. 100 c.c. of the hot filtered solution is treated with a mixture of equal parts of 40% formaldehyde, concentrated hydrochloric acid and water,[59] and boiled for 30 minutes under

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[56] *L. T. R.*, 1917, Oct. 10.

[57] *J. A. L. C. A.*, 1917, 344.

[58] *Z. angew. Chem.*, 1916, **6**, 325, 333; *J.*, 1916, 1028.

[59] Strasny, *J.*, 1906, 275.

a reflux condenser. After cooling, the solution is filtered and concentrated and tested as follows.

(a) Hydroxyazo reaction. 5 c.c. of the concentrated solution is treated with excess of alkali, cooled with ice, mixed with about half its volume of alcohol, and three or four drops of a solution of diazotised *p*-aminophenol added. A blue coloration indicates the presence of neradol D.

(b) Indophenol reaction. 5 c.c. of the above concentrated aqueous extract of the leather is treated with a drop of solution of the hydrochloride of dimethyl-*p*-phenylenediamine (obtained by reduction of methyl orange). The mixture is made alkaline with caustic soda, and treated with one or two drops of a 5% solution of potassium ferricyanide. A blue coloration indicates the presence of neradol D.

For the detection and differentiation of vegetable and synthetic tannins see also Laufmann (Chem. Zeit., 1917, **41**, 273; *J.*, 1917, 513).

Physical chemistry. Quite a number of important contributions have been made to this division during the past year, the true bearing of which on practical tanning is not yet clear; there is, however, no possible doubt that such work will in the future enable us to make progress far greater and with more safety than in the past. Procter and his pupils have recently shown that much which has been attributed to the surface-action implied in the name "capillary chemistry" is really subject to more general laws, and can be fully explained by mass action, electro-chemical attraction, and osmotic pressure.[60]

H. R. Procter has given a general review of the colloid chemistry of tanning in the recently issued Report of the British Association. The review is accompanied by a complete bibliography, which will prove of the greatest use to all chemists, not alone those engaged in tannery practice. The review is a concise account of our knowledge of the tanning process up to date, and should be read and studied in its entirety. Full use of it is made here.

The researches on the swelling of gelatin have been carried on by Procter[61] for a number of years, and have led to very important results, which are applicable not only to the processes of tanning, but also to general physiological processes taking place in the living body.

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[60] "Colloid Chemistry of Tanning." *Brit. Assoc. First Report on Colloid Chemistry and Its Industrial Applications*, 1917, p. 5.

[61] *Chem. Soc. Trans.*, 1914, **105**, 313; *J.*, 1914, 326.

Procter and Wilson (see list of papers 1, 4, 5, and 6, also Report, 1916, 230), in their work on the equilibrium of dilute hydrochloric acid and gelatin, have derived quantitative equations which explain the swelling and contracting actions of electrolytes on colloid jellies, as well as the various effects of adding electrolytes to sols. The derived formulæ apply to the whole colloid state, and therefore in themselves offer a quantitative explanation of the mechanism of tanning.

Vegetable tannage appears to be of a more colloidal or physical character than alum or chrome tannage. Tannins, like the proteins, appear to form colloidal rather than true ionic solutions, and the particles are negatively charged, passing to the anode in electrophoresis. Whether the charge is due to ionisation or to the fixation of an electrolyte ion is immaterial for our purpose. The gelatinous fibres take a positive charge in acid and a negative one in alkaline solutions; hence in faintly acid solution, which produces the strongest positive charge, they attract and precipitate the tannin particles, while in alkaline solution no tannage takes place, and in those too strongly acid the tannins themselves are precipitated,[63] in fact, such colloid precipitations, due to electric charges, do not seem to differ in principle from ionic reactions, though, owing to the varying size of the particles, and of their charges, they are less definite and quantitative. Whether ultimately any closer combination with the fibre ensues, as is suggested in the case of mineral tannages, remains for the present uncertain, but in long-continued tannage there is a further deposition of difficultly soluble matters on and between the fibres by forces generally called "adsorption."

Proteins, among which gelatin must be included, are now known to consist of open or closed chains of amino-acids, in which the carboxyl group of one is linked to the amino group of the next with elimination of the elements of water. In closed chains, groups within a single molecule having a terminal amino and carboxyl group, also give rise to similarly united ring structures. In this case the molecule is electrically neutral, and non-reactive till the ring is broken, while the open chains are amphoteric, basic by their terminal amino group, and acid by their carboxyl. A very useful practical distinction is that ring proteins are unattacked by trypsin alone, while pepsin is able to open the ring.

Gelatin can be digested by trypsin, but collagen is only attacked by pepsin, hence the view, supported by other facts, that collagen is

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[62] *Chem. Soc. Trans.*, 1916, **109**, 1327; *J.*, 1917, 92.

[63] *Chem. Soc. Trans.*, 1916, **109**, 1329; *J.*, 1917, 92.

the ring or anhydride form of gelatin into which it is converted by continuous boiling or by the action of acids or alkalis.

Procter found that when gelatin is placed in a solution of hydrochloric acid, the maximum swelling, which may reach an absorption of 50 c.c. of liquid for one gram of dry gelatin, occurs at an acid concentration under 0·005 N, from which it rapidly falls in a curve of hyperbolic type as the concentration is increased, the equilibrium being completely reversible up to about 0·25 N, beyond which some secondary reaction, probably a further breaking up of the proteid chain, begins to take place. At the same time the total absorption of acid steadily increases with concentration in a curve which may be closely represented by the ordinary adsorption formula $a = kx^{p}$ where a is the total acid, x the concentration of the external solution, and k and p are constants, but which is really due to a complicated osmotic equilibrium.

Gelatin, being amphoteric, acts as a very weak alkali in presence of hydrochloric acid, and forms a gelatin chloride, which like most salts is highly ionised (in fact to practically the same extent as hydrochloric acid itself). The base, however, is very weak, its ionisation being of the same order as that of water, and consequently the salt is largely hydrolysed, and can only exist in the presence of free acid. This gelatin base, gelatin chloride, and free hydrochloric acid are necessarily present in such a jelly in proportions determined by the concentration of the acid, and instead of a definite point of neutrality such as is given by a strong base, there is only a curve approaching, but never reaching, complete neutralisation. This is the explanation of the apparent indefiniteness of protein compounds, which has led many chemists to deny the existence of definite protein salts. By determining the hydrolysis curve and calculating the upper limit to which it tends, it is possible to calculate quite definite combining equivalents. Procter[64] in this way, on the assumption that gelatin had a second valency negligible at low acid concentrations, found a combining weight of 839, while Wilson,[65] from the same experiments, but regarding the apparent second valency as due to incipient decomposition or experimental error, found 768. It is not to be supposed, however, that these comparatively low weights represent the real complexity of the probably polymerised molecule in aqueous solution, but merely the smallest molecular division chemically possible.

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[64] *Chem. Soc. Trans.*, 1914, **105**, 320; *J.*, 1914, 320.

[65] *J.A.L.C.A.*, 1917, **12**, 108.

J. A. Wilson has published some of the results of his work,[66] which brought about a discussion on theories of leather formation (9) in which the chemical and adsorption theories were criticised from the point of view of the practical tanner. More recently H. G. Bennett,[67] in an able review of the present state of the theory of tanning, gives reasons for pinning his faith to the adsorption theory. He calls attention to the influence of the "lyotrope" series on the operation of tanning. Recent investigations have shown that the physical properties of water are affected by dissolved substances in a definite sequence. For instance, values of the surface tension and viscosity are affected by salts with the same cation in the following order:— $CO_3 > SO_4 > Cl > Br > NO_3 > I$. The cations have a similar sequence of effects when salts of the same anion are chosen: $Mg < NH_4 < Li < K < Na < Rb < Cs$.

In this connection E. Stiasny communicated to the writer several years ago a useful table showing the influence of successive series of anions and cations on the various processes involved in tanning. The table is here reproduced in the hope that it may contribute to the fuller understanding of the points to which Bennett[68] has called attention. The direction of the arrows indicates the succession.

Succession of Anions.

$CNS' - I' \quad Br' \quad ClO_3' \quad NO_3' \quad Cl' \quad C_2H_3O_2' \quad C_4H_4O_6'' \quad C_6H_5O_7''' \quad PO_4''' \quad SO_4''$ Increase

← - Swelling of gelatin (by salts)

← Solubility

← - - Melting point

- - → Precipitation of [illegible] emulsion colloids

← Precipitation of [illegible] emulsion colloids

- - → Increase of speed of ester catalysis (by $H^{\cdot}$) by addition of salts.

← - — Increase of speed of ester catalysis (by OH') by addition of salts.

← - Solubility of CO_2, H_2, H_2S, C_2H_5OH, $CH_3COOC_2H_5$, &c. (by salts)

← - - Compressibility of salt solutions.

→ Viscosity of salt solutions.

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[66] *J. Amer. Chem. Soc.*, 1916, **38**, 1982. See also Nos. 5, 6, and 9 in list of papers, p. 371.

[67] *J. S. L. T. C.*, 1917, 1, 30, 169.

[68] Procter remarks with regard to Bennett's arguments, that his statement that colloidal precipitation is electrical and not chemical would be equally applicable to every ionic action.

Succession of Cations.

$NH_3{}' — Ca'' — Ba'' — Na' — K'$

→ Swelling and plumping of hides.

← Hair loosening action

Wilson,[69] in a note on adsorption, calls attention to the fact that if the theory of colloids developed by Procter (v. s.) is correct, it must explain negative as well as positive adsorptions. He considers that it does this.[70]

The following papers on physical chemistry in relation to leather industries may be referred to:—

(1) Theory of Vegetable Tanning. H. R. Procter and J. A. Wilson. Chem. Soc. Trans., 1916, **109,** 1327; J., 1917, 92.

(2) The Equilibrium of Gelatine and Acid. R. Wintgen. Coll., 1916, 301/2, Coll. (Lond.), 1917, 43 (abstract).

(3) Swelling of Hides in Presence of Hydrogen Ions. G. Povarnin. J. Russ. Phys. Chem. Soc., 1915, **47,** 2064; Coll. (Lond.), 1917, 45.

(4) Theory of Colloids. J. A. Wilson. J. A. L. C. A., 1917, 122; Coll. (Lond.), 1917, 97.

(5) Note on Adsorption. J. A. Wilson. J. A. L. C. A., 1917, 126; Coll. (Lond.), 1917, 100.

(6) Theories of Leather Chemistry. J. A. Wilson. J. A. L. C. A., 1917, 108; Coll. (Lond.), 1917, 105.

(7) A Theory of Vegetable Tannin Colloids: their Constitution and Mode of Action. W. Moller. Ledertech. Rundl., 1915. J., 1917, 225.

(8) The Sol and Gel Condition of Gelatin Solutions. L. Arisz. Koll. Chem. Beihefte, 7, 1915, Heft 1/3, 1/90, full abstract by Professor H. R. Procter, in J. S. L. T. C., 1917, 45.

(9) Discussion on Theories of Leather Formation. J. A. L. C. A., 1917, 450.

(10) Action of Neutral Salts upon Chrome Liquors. J. A. Wilson and E. J. Kern. J. A. L. C. A., 1917, 445; J., 1917, 1140.

(11) Osmotic Pressure of Gelatin. W. Bilz, G. Bugge and L. Mehler. Z. phys. Chem., 1916, **91,** 705–712; J., 1917, 297.

(12) Tanning Phenomena in Jellies. W. Moeller. Kolloid Zeit. 1916, **19,** 205; J., 1917, 465.

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[69] *J. A. L. C. A.*, 1917, 126.

[70] *J. Amer. Chem. Soc.*, 1916, **38,** 1982.

(13) Hydratation and Dissolution of Gelatin. M. H. Fischer. Koll Zeit, 1915, **17**, 1 7. J., 1916, 265

(14) The Adsorption of Chrome Oxide by Hide Powder A. W. Davison J A L C A, 1917, 258

American leather chemists have now, in conjunction with the U.S. Tanners' Association, founded a research laboratory of their own. The laboratory is in the Pratt Institute, New York, and the first director is Mr Jesse Briggs Churchill

Articles of special interest to tanners, in which the relations of the chemist to works are discussed from a practical standpoint, are "Chemistry and its Relation to Tanning," by G T Laemmle,[73] and "Chemical Control in the Tannery," by J G Greaves[74] It is pointed out, rightly, that in connection with the purchasing of materials alone every tannery could afford its own laboratory Removing the personal element out of the purchasing also removes a lot of doubt and saves a lot of selling expense. Some firms use high-priced classes of materials in certain processes where cheaper ones would do as well

GLUE MANUFACTURE

The enormous advance in aeronautics has brought with it an increased demand for the best glues, which are required for joining together the laminae of aeroplane propellers P A Houseman[75] gives an empirical method for testing the quality of the glue used for this work. Pieces of straight-grained walnut wood, each 9 in by 2 in. by ⅜ in., are dried at 36 C for 24 hours, then roughened by a tooth-plane, and two of the pieces are glued together so that their ends overlap by 2 in ; the area of the glued surface is therefore 4 sq in. The glue is prepared by soaking the pieces for about 18 hours in water, then heating the mixture to 60° C and applying it at this temperature ; usually, one part of glue to two parts by weight of water gives a suitable concentration. The joint is clamped under moderate pressure for 48 hours and tested after a further 24 hours, the tests, in duplicate, being made as follows: *Regular test* The joints are pulled apart in a testing machine, and the breaking strain per square inch of glued surface is recorded. *Heat test* The joints are heated at 45° C for two days and then pulled apart, and the breaking strain recorded

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[73] *J A L C A*, 1917, 169

[74] *Ibid* 1917, p 337

[75] *J Ind Eng Chem*, 1917, **9**, 359, *J*, 1917, 513

Immersion test. The joints are completely immersed in water at 20° C. for 12 hours and then pulled apart. Results of from 150 to over 600 lb. per square inch of glued surface are found in the regular test, and about the same figures in the heat test, whilst the immersion test results are sometimes lower, and sometimes higher, than the regular test results. The addition of a small proportion (5%) of phenol to the glue solution increases the strength of the joint; addition of ammonia does not affect the regular test results but raises the heat and immersion test figures. A Swiss casein glue, of the type used on German aircraft, and consisting of about 66% of casein, 23% of mineral matter (sodium salts, silica, lime and alumina) and 1% of petroleum, gave a particularly high result in the immersion test.

F. H. Stevens[74] patents the use of formaldehyde for waterproofing glue joints. The surfaces to be joined are moistened with a solution of formalin (25% of 40% formaldehyde) and are then covered with glue in the usual way.

O. Rohm[75] patents the use of pancreatic or similar enzymes which are capable of splitting up or digesting albumin. Instead of the preliminary extended treatment with lime, followed by washing and neutralisation with hydrochloric acid, the glue pieces are treated for a few hours with the enzyme solution. After the pieces have been treated in this way they are boiled in the usual manner.

An attempt to ascertain the chemical differences between fish gelatin and bone gelatin has been made by Y. Okuda.[76] Fish gelatin derived from shark skin was hydrolysed with hydrochloric acid, baryta, and sulphuric acid, and the products from each investigated. The total nitrogen and its distribution was found to be the same for both sorts; but the fish gelatin gave rather more monoamino acid, and much more glycocoll, alanine, leucine, phenylalanine, glutamic and aspartic acids than the bone gelatin. The proline and serine contents of the fish gelatin formed by the ester method were low, probably the results of experimental errors. The diamino acids were present in about equal quantities in the two gelatins.

In the manufacture of bone glue R. Berliner,[77] Moscow, patents a process in which the bones are treated with sulphur dioxide; the fat is then extracted, and at the same time the sulphur dioxide is expelled, after which the glue is boiled out.

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[74] Eng. Pat. 106439; *J.*, 1917, 728.

[75] Eng. Pat. 104181; *J.*, 1917, 1141.

[76] *J. Coll. Agric. Tokyo*, 1916, **5**, 355–363; *J.*, 1917

[77] U.S. Pat. 1176644, 1916; *J.*, 1916, 551.

The chemical analysis and investigation of glues has been neglected in this country, except for the work of Rideal and Trotman. Very useful information on the analysis of glue is given by the latter in his book "Leather Trades Chemistry" (Charles Griffin & Co., Ltd., London, 1908), p 238, and by the former in "Glue and Glue Testing" (Scott Greenwood & Co., London, 1900), p. 107. Some of the larger glue works employ competent chemists, but very little of their work is published.

SUGARS, STARCHES AND GUMS

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PART I. SUGARS

THE CANE SUGAR INDUSTRY

Agriculture A novel method of destroying weeds in the cane fields developed by Eckart[1], is based on the fact that the young cane-shoots can pierce an overlying covering of thick paper or similar material Weeds fail to penetrate, and therefore wither and die The paper covering also acts as a mulch in conserving soil moisture, and can be transported from field to field The paper may be impregnated with tar in order to absorb the sun's heat, causing the temperature of the covered soil to be from 3½° to 6° higher than that of the adjoining uncovered soil This elevation of temperature stimulates nitrification and assists the vigorous growth of the cane-shoot

Manufacture—During recent years, the extraction of cane juice by milling has been increased by about 3 in certain Hawaiian factories, an extraction of 98 of sucrose present in the cane being obtained at the Ewa factory. This excellent result is due to two mechanical improvements, namely, the Messchaert system of grooving the mill-ollers, and the Searby shredder, which prepares the cane for the milling operation The Messchaert grooving provides a free outlet or the extracted juice at the point of maximum compression of the ane-fibre between any pair of rollers, the juice flowing inside the rooves, and therefore out of contact with the compressed blanket of ibre passing between the rollers The grooving was first applied to he front, or "feed-roller," but has also been applied with success to he back, or "discharge roller."

The Searby shredder consists of a horizontal shaft driven at a high peed, and carrying beaters or hammers, which drive the entering cane gainst a series of horizontal rigid bars lying just beyond the circuit nade by the revolving beaters. The sharp edges of these bars tear he cane into threads, but without extracting any juice The shredded naterial then gravitates to the mill where the juice is extracted

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[1] *Intern Sugar J* 1917 455 457

The capacity or output of cane mills has been increased by another type of grooved roller, designed to grip the entering feed of fibre, thus eliminating "slip." In the Hind-Renton patent[2] the sides of the grooves form an angle of 30°–35°, and mesh with similar grooves in the adjacent or co-acting roller. The fibre under treatment is thus wedged into the grooves on one roller by the corresponding ridges on the co-acting roller. As this gripping action is independent of the texture of the roller surface, the rollers may be made of steel. Other inventors have attempted to combine this type of grooving with the Messchaert juice-grooves, thus securing increased capacity and extraction.

A method of measuring mill efficiency, based on the composition of the crushed cane or "bagasse," was proposed by Lely in 1911. As this value depends very largely on the quantity of maceration water applied during milling, he has now introduced a "universal figure for mill performance,"[3] in which the amount of sucrose lost in milling is multiplied by a factor representing the excess of maceration water applied over the standard quantity used in Java.

In the Hinton-Naudet process of extracting the juice, the canes are first crushed in a mill, and the resulting juice (after liming and heating) is filtered through the bagasse in a diffusion battery, after which the juice is washed out of the bagasse by water in the same manner as in the diffusion of sliced cane or beet. This process was first applied to the cane in Madeira, where it is still employed. It was also tested on a larger scale in Trinidad, Porto Rico, and Cuba, but with less satisfactory results.

Recent improvements[4] of this process include: (*a*) Forced circulation of the juice under constant volume and at a high temperature (110° C.); (*b*) Merchage at a lower temperature (80° C.); and (*c*) Juice drawn off into the measuring tank at any suitable temperature.

The following improvements relate to the chemical treatment of the extracted juice.

Fribourg[5] proposes a mixture of kieselguhr and dicalcium phosphate (2 : 1) added in the proportion of 3 to 5 kilos per 1000 litres of juice after the usual liming and sulphitation, permitting the whole of the juice to be filter-pressed, instead of the usual subsidation and filter-pressing of sediment. The filtering surface required is 50 sq. m. per 100 tons of cane treated.

A new clarifying agent phospho-gélose patented by Guerrero, consists approximately of 70 phosphates of lime (chiefly dicalcium phosphate) and 30 keiselguhr and other products. Investigations by Fribourg[6] gave the following results. Filtration of the whole of the treated juice was practicable. The weight of dry filter cake obtained per 1000 litres of juice was from 11 to 12.5 kilos as compared with about 6 to 8 kilos by the ordinary treatment with lime and sulphur dioxide. All the phosphoric acid added, together with that present in the original juice is recovered in the filter-press cake, which, therefore, represents a valuable manure, including nitrogenous matter.

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[2] Eng. Pat. 1372 (1915).

[3] *Intern. Sugar J.*, 1916, **18**, 323.

[4] Fr. Pat. 466590 (1913), Eng. Pat. 5650 (1914), *J.*, 1916, 321.

[5] *Bull. Assoc. Chim. Sucr.*, 1916, **33**, 227–255; *J.*, 1917, 152.

Adams,[7] of Hawaii, has conducted factory experiments to ascertain the possible advantages of treating separately, the rich juice extracted by the first mill, and the dilute juice extracted by saturation and re-crushing in the following mills.

The time required for subsidation was reduced, also that of boiling in the vacuum pan. The dilute juice contained less reducing sugar, but 45 more ash, and 79 more gum than the rich juice extracted by the first mill, when calculated to the same degree Brix. Special chemical treatment might be adopted to remove these impurities from the dilute juice. Lime and phosphoric acid gave good results.

This mode of working has been further elaborated by Truscott.[8] The purer juice, extracted by the first mill and crusher, is limed separately from the more impure and dilute juices extracted by the following mills, the quantity of lime being adjusted to secure the maximum purification of each juice. The later juices are allowed to subside after liming and heating, and the clarified liquid is then mixed with the richer and purer first mill juice before the latter is heated and subsided. The mixed juice is then treated in the usual manner.

Deschamps[9] has designed a process for manufacturing sodium hydrosulphite in the raw sugar factory or refinery. Zinc hydrosulphite is first prepared from zinc and sulphur dioxide and then treated with caustic soda. The main feature of this process is the production of sulphur dioxide gas entirely free from oxygen, by means of a special sulphur-furnace. The necessary plant is not costly.

The carbonatation process for the manufacture of white sugar direct from the cane is used in Java, and a few other countries where suitable limestone is obtained locally. Weinrich[10] has modified this process by adding the lime in the form of dry powder to a thick magma of low grade sugars and raw juice. The dry caustic lime acts more energetically on the colouring matter and impurities than does milk of lime, and, by working at lower temperatures, the destruction of glucose is avoided. After liming, the magma is dissolved in sufficient raw cane juice, and carbonated in the usual manner. About 80% of the colour and 50% of the total impurities can be removed. An interesting feature of the process is the possibility of the raw sugar factory working as a refinery between the usual grinding seasons, converting its own raw sugar (or purchased raw sugar) into white granulated sugar, without requiring additional plant.

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[6] *Bull. Assoc. Chim. Sucr.*, 1916, **33**, 244-255.

[7] *Intern. Sugar J.*, 1916, **18**, 118-119.

[8] U.S. Pat. 1177832 (1916); *J.*, 1916, 647.

[9] *Intern. Sugar J.*, 1916, **18**, 182.

[10] U.S. Pat. 1084771 (1914); *Intern. Sugar J.*, 1917, 450; *J.*, 1914, 211, 1917.

Attempts have been made to substitute centrifugal separation for filtration in clarifying the juice after chemical treatment, the following advantages being claimed: (*a*) As the separated solid matters (scum) do not retard the escape of clear juice, the separation takes place at a uniform speed; (*b*) There being no filtering medium, the working expenses are small; (*c*) Less labour is required to operate a battery of centrifugals than an equivalent number of filter-presses. Experiments in this direction were first made by C. Matthey in a Russian beet factory. Heriot's juice-centrifugal, patented in 1897, has been followed by about ten different patents, of which the Kopke separator is probably the best known.

Kerr[11] has studied various types of multiple-effect evaporators with the following results, expressed as pounds of water evaporated per square foot of heating surface per hour, assuming steam pressure of 5 lb. per sq. in. in first body, and a vacuum of 26 inches in last body.

A. Vertical submerged tubes (standard type), double effect, 16·7 lb.; triple, 9·2 lb.; quadruple, 6·18 lb.

B. Horizontal steam tubes, triple effect, 11·19 lb.; quadruple, 4·55 lb.

C. Horizontal film evaporator, quadruple effect, 11·05 lb.

D. Vertical film evaporator, triple effect, 9·21 lb.; quadruple, 10·05 lb.

E. Standard type (A), with special baffle steam distributor working under vacuum, triple effect, 16·93 lb.

F. Same as (E) but working under pressure, double effect, 17·40 lb.

G. Vertical double steam tubes, quadruple effect, 9·67 lb.

From Kerr's experiments[12] in Louisiana and Porto Rico, the average coefficient of heat transmission in vacuum pans, when boiling unmixed strikes, was 110. With pans having short coils, the higher values 124·3, 134·5, and 174·8 were obtained. Excluding these three, the average for coil-pans was 95. Calandria (Express) pans gave values about 40 higher than for coils.

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[11] *Met. and Chem. Eng.*, 1916, **14**, 603–608; *J.*, 1916, 601.

[12] *Intern. Sugar J.*, 1916, 21; *J.*, 1916, 190.

Naudet's evaporator with "juice circulator" (see p. 384) has been tested in a Cuban cane sugar factory, giving an increase of 10·4 in evaporating power.

A new principle is adopted in the Soderlund and Boberg systems[13] of "evaporation by thermo-compression." The vapour evolved from the boiling liquid in a single vessel is heated by compression and returned to the heating surface of this vessel, thus causing additional evaporation. As the compressor operates continuously, the vapour evolved by the boiling liquid continues to supply the necessary heat, and is condensed on the exterior surface of the heating tubes.

In the manufacture of finely powdered sugar Shaw and Baker[14] pass syrup through a steam-heated spiral until it attains a temperature of 270° F. It then enters a horizontal stirring apparatus, where it is crystallised by diluting with 10 to 40 syrup at 120° F., forming a finely grained dry mass. By varying the temperature and amount of cooling syrup, the size of the crystals may be regulated.

Williams,[15] of Hawaii, claims to have demonstrated that the sucrose present in waste molasses can be recovered by merely evaporating the water present, thus proving that water is the only factor which prevents the sucrose from crystallising. After concentrating molasses to 99 Brix, and then slightly diluting with water, the crystallised material is treated in a high-speed centrifugal with imperforate drum, and thereby separated into two layers. The outer layer (nearest the drum) contains the major portion of the sucrose crystals and a minor portion of impurities. The interior zone, or belt, contains a minor portion of the sucrose and a major portion of impurities. The outer belt contains 45 of the sucrose originally present, and, by analysis, gives 50 polarization and 53 purity. It is dissolved in water to form a syrup, boiled in the vacuum pan and crystallised in the usual manner.

The figures given by Williams have been criticised by Geerligs[16] who shows that, although about 4 of the sugar contained in Hawaiian waste molasses can be recovered by Williams' process, such extraction is due to the fact that what is technically termed "waste molasses" generally contains a small quantity of crystallisable sucrose, which might have been recovered by the usual methods of evaporation and cooling He considers the Williams process costly and irrational, compared with the modern methods adopted in Java, and that it fails to support the claims of its inventor.

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[13] *Times Eng. Supp.*, Dec. 29, 1916; *J.*, 1917, 71.

[14] Eng. Pat. 2851 (1915); *J.*, 1916, 432.

[15] *Intern. Sugar J.*, 1917, 19, 90; *J.*, 1917, 398.

[16] *Intern. Sugar J.*, 1917, 159–161.

By-products Cane molasses contains about 9 ash, of which from 25 to 30 is potash The recovery of this potash requires a special type of furnace, and the heat evolved may be utilised for steam raising purposes in the sugar factory, thus supplementing the main fuel—bagasse

Tucuman molasses ash contains from 15 to 50 K_2O, corresponding to 66 to 75 K_2CO_3 Cross and Harris[17] propose to purify this ash by fractional crystallisation. They also utilise vinasse (spent wash) from molasses as a source of potash The vinasse is partially concentrated, acidified with sulphuric acid then evaporated to dryness, yielding a dry black powder suitable for transport in bags or barrels By concentration without sulphuric acid a pasty hygroscopic substance results

Molasses can be applied to the soil direct, or after mixing with other materials Herzka adds from 30 to 50 of its weight of ground mineral phosphate, and treats the mixture with sufficient sulphuric acid to decompose the phosphate and to convert the potassium carbonate in the molasses to sulphate

A substitute for petrol is manufactured from fermented molasses in Natal, under the name " Natalite "[18] which is a mixture of alcohol and ether. Experiments made by the late Professor V B Lewes showed that the vapour pressures of alcohol alone at temperatures from 60 to 100° F are below those of Pratt's " Perfection " petrol spirit, whereas those of " Natalite " are higher A motor-car engine could be started with the greatest ease with " Natalite " even at a low temperature With a speed of 1300 revolutions per min 1 17 gallons of " Natalite " gave the same result as 1 gallon of best petrol

Breckler[19] states that alcohol can be produced from " black strap " molasses at a cost of 10 cents per proof gallon, but it is estimated that the total raw material available in U S A. and Cuba would produce only 162 million gallons of alcohol, or 5 of the total requirements for motor fuel During 1915, the demand for cheap alcohol for the manufacture of smokeless powders has greatly increased the demand for cane molasses, raising the price of the latter to 15 cents per gallon.

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[17] *Rev Ind y Agric de Tucuman*, 1916, 7, 95 103, *Intern Sugar J*, 1917, **19**, 281 283

[18] *Chem Trade J*, June 19, 1915, *J*, 1915, 705

[19] *J Ind Eng Chem*, 1917, **9**, 612, *J*, 1917, 902

Where molasses is not converted into alcohol on the spot it may be evaporated to a solid material for shipment abroad. In 1913, over 66,000 tons of solidified molasses were produced in Java, and in 1914, over 96,000 tons, the output of sixty-three factories.

A Cuban sugar factory is manufacturing paper from the crushed cane or "bagasse" leaving the mill.[20] The paper factory adjoins the sugar factory, and employs twenty-five men producing four tons of paper per day. Three kinds of wrapping paper are produced, and new machinery is being erected for the manufacture of all grades of paper.

The manufacture of wrapping papers has also been successfully carried out at Preston Sugar Mill, Cuba,[21] during 1915. The output is consumed locally, and the manufacture of other grades of paper will shortly be undertaken. The bagasse is digested with live steam and transferred to beaters, where it is mixed with bleaching powder. After beating, it is thinned with water before entering the paper machine.

Cane wax is extracted from filter press cake by means of benzol in several factories in Natal. The Uba variety of cane gives filter-cake containing from 11 to 17 wax. The crude wax is dark in colour and requires further purification, which is said to be costly. Clacher[22] has extracted the wax in a purer form by means of kerosene. The crude wax melts at 72.5° to 76.5° C., and bleached wax at 71° to 76° C. It is a suitable substitute for carnuba wax.

Salamon[23] bleaches this wax by melting it over water containing potassium chlorate and dilute sulphuric acid at a temperature of 70° to 100° C., air being blown through the molten wax for several hours.

The Beet Sugar Industry.

Agriculture. Experiments were carried out in Ireland[24] during 1912 and 1913 to compare the yield of roots per acre and saccharine richness when cultivated in rows on the flat (continental method) and on moulded-up drill rows. The former system gave a yield of only 14 to 17 cwt. higher, and a sucrose content only 0.3 to 0.7 higher than the latter system The beet were grown alongside mangolds, the relative yields being as follows:

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[20] *Intern. Sugar J.*, 1916, **18**, 252.

[21] *J. Roy. Soc. Arts*, 1915, **64**, 132; *J.*, 1916, 39.

[22] *Int. Sugar J.*, 1916, **18**, 22.

[23] Eng. Pat. 5060 (1915); *J.*, 1916, 609.

[24] *J. Dept. Agric. and Tech. Inst. Ireland*, 1914, **14**, 471-482.

Beets (gross weight)	17 tons 9 cwt. per acre.
Beets (factory weight)	13 tons 10 cwt. per acre.
Mangolds	28 tons 18 cwt. per acre.

Thus the factory weight of sugar beet was only about half that of mangolds

The average yield of washed roots in Norfolk and Suffolk[25] is 12 tons per acre, and the cost of growing, including seed, manure, cultivation, rent and rates is £9 7s 8d per acre The price of roots in 1914 was 25s. per ton f.o.r A crop of 12 tons will thus give the farmer £15, and a profit of £5 12s 4d per acre

In Northumberland and Durham[26] the yield of washed roots was 7·5 tons per acre, and the average sucrose content 15 20 The sucrose varied from 12 ; to 16 8 .

In a paper on "The Sugar Beet its Cultivation and Financial Aspects," by R. N. Dowling, published by the "Journal of the Farmers' Club," in 1915, some hundred field trials, on all classes of soils, in the West of England, gave the following average results Yield of topped and washed roots 12 tons per acre; percentage of sugar in the roots = 18·0; and purity of the juice 92 0 In South Wales, the average yield of washed roots was 15 tons per acre.

The results of field-trials in the South-West of Scotland, during 1917, have been published in a Report by Prof R A Berry, the averages being as follows Yield of topped (unwashed) roots = 9 3 tons per acre; yield of sugar in the roots 1 46 tons per acre; percentage of sugar in the roots = 15 71 , and purity of the juice 87 3

The sugar beet can be profitably cultivated in widely different parts of Canada[27] During 1913, the highest sucrose content was 17·86 and the lowest 13 40 At the experimental farms it averaged 17 , the juice having a purity of 90 The seed used was of three varieties, Vilmorin's Improved A Vilmorin's Improved B, and Klein Wanzleben.

M. Potvliet[28] records some interesting particulars in a paper on "The Beet Sugar Industry in Canada" The average yield of roots per acre is 10 tons, but yields of 18 tons are not uncommon. Before the war, the price of imported seed was about $10 per 100 lb, but has now risen to $25 and higher. Home grown seed is very scarce.

[25] *J Board Agric*, 1915, **21**, 969-987

[26] *J*, 1913, 929-931

[27] *Rep Dept of Agric Canada*, 1913, 242-245

[28] *J*, 1916, 143-144

In Utah, U.S.A., experiments have been made to raise seed on a large scale, with some success, and the Dominion Sugar Company is also experimenting near Berlin, Ontario. In 1915 Canada produced about 35,000 tons of beet sugar and imported about 300,000 tons, partly cane sugar from Cuba and West Indies and partly raw beet sugar from Europe. Canada should produce all the sugar she consumes. The Province of Ontario, with 285,000 sq. miles, has only three beet factories, whereas Holland, with only 12,600 sq. miles has twenty-eight factories. The increased yield of other crops, grown in rotation with beet in Colorado and California, were as follows: Wheat 21 , rye 45 , barley 25 oats 12 , peas 86 , and potatoes 102 .

The Canadian soil contains 0·35 of potash, or 11,000 lb. per acre-foot. Of this total, 150 lb. is available. The available phosphoric acid is 150 lb. per acre-foot, and a beet crop of 12 tons per acre removes only 19 lb. The amount of available nitrogen is not so abundant, but is made good by crop rotation.

Stoklasa's[29] investigations on the growth of the sugar beet led to the following conclusions. In an atmosphere free from carbon dioxide, plants can produce proteins during sunshine both in the presence and absence of potassium, when dextrose, levulose or sucrose is added as a source of carbon. This synthesis can also take place when no sugar is added, if the plant contains sufficient reserve organic material. In the absence of light, a similar synthesis of proteins can occur when the source of nitrogen is a nitrate and the source of carbon a carbohydrate, but only in the presence of a potassium salt. The author refers to other researches which indicate the part played by potassium in the assimilation of carbohydrates.

Experiments by Munerati, Mezzadroli, and Zapparoli[30] on the sugar content of single beets at different stages of growth and the distribution of the sugar in the root gave the following results. In all cases the smallest differences in sucrose distribution (rarely exceeding 0·5) occur in the pulp, normal to the axis in the upper third of the root, below the neck. Changes in the sugar content of beets during growth do not follow any definite rule. The analysis of a beet at any given time affords no criterion of its sugar content at some other period.

The loss in weight of roots when piled in the field has been determined by Shaw.[31] Experiments in Utah, with open piles of 1 to 3 cwt. of topped roots, gave a loss of 4·7 in twenty-four hours at a mean temperature of 43° F. In Kansas, an average daily loss of 6·48% was found during four days, at temperatures between 4° and 67° F. Open piles of about 5 cwt. of topped roots showed an average daily loss of 2·9% in five days, at a mean temperature of 47° F. Similar piles, protected by a covering of beet tops, gave an average daily loss of 0·9%. The loss of sucrose appears to be practically negligible when stored under the above conditions for a few days.

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[29] *Biochem. Zeits.*, 1916, **73**, 107; *J.*, 1916, 700.

[30] *Staz. Sperim. Agr. Ital.*, 1915, **48**, 605—637; *J.*, 1916, 373.

[31] U.S. Dept. Agric., Bull. No. 199, April 7, 1915, p. 12; *J.*, 1916, 61.

Manufacture. The Naudet system[32] of diffusion with forced circulation was first applied in the beet sugar factory with marked success, and subsequently applied to the extraction of sugar from the cane (see p. 379). The forced circulation during diffusion of beet ensures a more uniform extraction of sucrose from the sliced beet, and a corresponding higher density of the juice drawn off from each diffuser.

Naudet[33] has also applied forced circulation during evaporation by multiple effect, without employing pumps for this purpose. The juice-inlet to each vessel is placed just above the upper tube-plate, and communicates externally with a juice-outlet at the bottom of each vessel, forming an external circuit. The juice entering each vessel (from the preceding vessel) passes through an injector placed in the external circuit, thereby causing an upward current of juice therein, and a corresponding downward current over the heating surface within the vessel. Additional heating surface may be secured by adding a vertical tubular heater to each exterior circuit, between the injector and the juice-inlet in each vessel.

Owsianikow[34] has introduced crystallisers with communicating pipes in such a manner that the massecuite added to the first vessel displaces an equal weight from vessel to vessel until it passes from the last vessel into the centrifugal "mixer." He claims the following advantages for his system over the present system of separate vessels:—(1) As the full capacity of the plant is utilised, a given quantity of massecuite remains longer under treatment; (2) The entire output of massecuite is more homogeneous and more easy to cure; (3) Too rapid cooling is avoided; (4) Boiling can be done in small pans, and therefore more rapidly.

By-products.—Beet-crowns without leaves can be used for feeding horses, sheep, and pigs.[35] The crowns and leaves form an excellent fodder for cows, if supplemented by other food. The leaves should be kept dry and clean. A silage can also be made. If artificially dried, the resulting fodder is equal to meadow hay.

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[32] Fr. Pat. 466596 (1913); *J.*, 1914, 879.

[33] U.S. Pat. 1190317 (1916); *J.*, 1916, 967.

[34] *Sugar*, 1916, **18**, 418.

[35] *Journ. Board of Agric.* 1915, **22**, 750–760.

A powdery fertilizer is prepared from beet-molasses by Wilkening. The molasses are mixed with peat, and inoculated with azotobacter, which decomposes the betaine. The treated mixture then contains about 25 water, 3·75 nitrogen, 9·75 potash, and 15·0 humus. Sufficient superphosphate may be added to cause the mixture to contain 3 phosphoric acid.

A company has been formed to manufacture potash salts from waste beet molasses of the Mason Malt Distillery Co, at Sausalito, California, U S A.

Herzka[37] prepares a fertilizer from waste waters (Steffen and Osmosis processes) of the beet sugar factory by concentrating to 55 Brix and treating with sulphuric acid, equivalent to the total lime and alkali present. Calcium superphosphate, nitrogenous animal refuse, and sawdust are then added, and the mixture dried

In 1904, France produced 13·8 million gallons of alcohol from beet molasses out of a total alcohol-production of 19·6 million gallons, or 27·8 from molasses. In the same year, Germany produced 2·45 million gallons of 95 alcohol from beet molasses out of a total production of 101·8 million gallons, or 2·4 from molasses During the war, German beet molasses have been used for the production of yeast[38] for foodstuff and fodder. The yeast employed for this purpose produces no alcohol, but multiplies twice as rapidly as distillers' yeast. It is grown in diluted molasses, containing added ammonium and other salts. The demand for this nutrient yeast for human consumption has led to the construction of plants capable of producing from 100 to 15,000 tons of yeast annually.

THE REFINING INDUSTRY

Decolorising carbons These possess a much higher decolorising power and are said to absorb more organic and mineral impurities from sugar solutions than bone-char. The mode of working also differs greatly from the customary practice in the refinery; filter presses of small capacity being substituted for the large bone-char filters or cisterns. Filter-pressing performs the double function of separating the carbon, after it has acted upon the liquor (so that it may be used again), and simultaneously removing all suspended impurities from the liquor,

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[36] *Int Sugar J*, 1916, 161

[37] U S. Pat 1212484 (1917); *J*, 1917, 398

[38] **Hayduck**. *Polytechn. Ges. Berlin*, 1915; *J*, 1916, 323.

thereby dispensing with the Taylor bag-filters now used. Further, the vegetable carbons can be revivified by chemical treatment, thereby dispensing with the kilns or furnaces required for bone-char If these carbons can be manufactured cheaply, it appears possible to combine the manufacture of raw sugar with the refining operation in the raw sugar factory. Raw sugar (cane or beet) would be manufactured during the crop season, and subsequently refined during the interval between the crop seasons, no additional machinery being necessary. This has already been done in two Dutch beet factories, working with "Norit" in the proportion of 2 % on the weight of raw sugar treated. The earliest patent for producing a very active decolorising carbon from wood appears to be that of Ostrejko.[39] Wood is treated with a solution of calcium or magnesium chloride, or with calcium acetate, before ignition out of contact with air

More recent patents are as follows :—

Bonnard, Rule, and Nicol, Eng. Pat. 10622, July 31, 1915, *J.*, 1916, 1212.

R. M. Catlin, U S. Pat. 1219138 (1917), *J.*, 1917, 195.

Investigations were carried out by a committee[40] of the Royal Society on the production of decolorising carbon, similar to the German and Dutch products "Eponite" and "Norit" It was concluded that "Eponite" is made from a mixture of coniferous wood, such as pine or cedar, and angiospermous wood, such as poplar or willow. Experiments were made on willow and cedar under the following conditions :—(1) Natural wood without treatment; (2) treated with milk of lime; (3) treated with calcium acetate. These were carbonised at a white heat in a salamander crucible heated in a Fletcher radial injection furnace. The resulting carbon was washed, first with hydrochloric acid, then with water, and finally heated. Process (1) gave charcoals useless for decolorising purposes, (2) and (3) gave very active charcoal, equal to "Eponite." The charcoals obtained after treatment with calcium acetate were slightly more active than those obtained after treatment with milk of lime, and the type of wood treated had little or no influence on the result.

Sauer claims that when washed raw sugar is treated with "Norit," 70 % of the colour is removed by 0·25 %, and 100 % of the colour by 3·0 %. Owing to the small quantity of water required to wash out the sugar liquor from the cakes of "Norit" in the filter-presses before the latter is revivified, and the suitability of these washings for "melting" fresh quantities of raw sugar, the normal fuel consumption of a refinery would be reduced by 25 on substituting "Norit" for bone-char.

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[39] Eng. Pat 18040 (1900)

[40] *Chem. Trade J*, 1917, Sept 15, p. 218; *J*, 1917, 1041.

Pellet[41] has studied the decolorising power of numerous carbons relative to Eponite taken as standard. His experiments were made with solutions of molasses, acidified with hydrochloric and sulphurous acids, prepared during the determination of sucrose by polariscopic methods. The carbons investigated gave different relative efficiencies in the presence of these two acids, the order of their activities being as follows:—(*a*) *Hydrochloric acid present*: Eponite, 1; Littoral, 2; Flandriac, 3; Flaming, 4; Special carbon for wines, 5; bone-char (fresh), 6; bone-char (washed with acid), 8; cherry-stone, 9. (*b*) *Sulphurous acid present*: Eponite, 1; Flandriac, 1; Littoral, 2; Special carbon for wines, 5; bone-char (washed with acid), 6; Flaming, 7; bone-char (fresh), 8; cherry-stone, 9.

Weinrich[42] criticises the claims in favour of "Norit," and regards all vegetable carbons as inferior to bone-char for large scale operations. He claims that bone-char removes as much colour as an equal volume of vegetable carbon, and, in addition, removes organic and mineral impurities not absorbed by vegetable carbons.

Vegetable carbons may also be used to facilitate filtration of refinery liquids. Wijnberg[43] employs 0·5 to 1 on the weight of sugar in solution. The liquor obtained from 100 tons of cane sugar, of 96 polarisation, after this treatment, required only 4000 sq. ft. of filtering surface. The same liquor, treated with 1 of kieselguhr, or with phosphate of lime, required 10,000 sq. ft., and, without any treatment, required 60,000 sq. ft. of filtering surface.

Murke[44] refines cane sugar without bone-char or other forms of carbon. Raw cane sugar is mixed with molasses to a thick magma, separated therefrom in centrifugals and purged with water. The washed crystals are dissolved in water to a syrup, and treated with milk of lime in the proportion of 0·5 to 2 CaO of the dry sugar present. After boiling, the syrup is carbonated until the alkalinity is reduced to 0·1 CaO, filtered, treated with sulphur dioxide until very slightly alkaline, and again filtered. The clear syrup is then boiled to massecuite in the usual manner.

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[41] *Bull. Assoc. Chim. Sucr.*, 1916, **33**, 220–227; *J.*, 1917, 153.

[42] *Int. Sugar J.*, 1917, 106–107; *J.*, 1917, 1106.

[43] Eng. Pat. 3854 (1915); *Int. Sugar J.*, 1916, 194; *J.*, 1916, 432.

[44] Eng. Pat. 6661 (1915); *J.*, 1916, 648.

MANUFACTURE OF SUCROSE FROM OTHER PLANTS.

Palm.—In India, about 10% of the home-grown sugar is made from palms, mostly from the wild date variety (*Phœnix sylvestris*) in Bengal, and from the palmyra palm in Madras. Palm gur is darker than cane gur, due to the alkalinity of the palm juice acting upon the reducing sugars during boiling. Annett[45] overcomes this by previously neutralising the juice with citric acid.

Sorghum.—Three practical methods of defecating sorghum juice have been studied by Anderson,[46] namely, (1) heating and skimming, without addition of lime, (2) defecation with lime, and (3) defecation with acid calcium phosphate (5 lb. per 1000 gallons). Method (3) gives rather better syrup than method (2), but, taking into account the cost of working, method (2) is considered preferable.

About 17 million gallons of sorghum syrup were produced in 1900 in the United States, and the industry has since then developed in certain districts. The average cost of production is estimated at 19 cents (9½*d.*) per gallon. Jordan and Chesley[47] give the following analyses:—Total solids, 71·6; ash, 2·1; sucrose, 40·0; reducing sugars, 28·1, gums and extractives, 1·0; and acidity (as tartaric acid), 0·8%. The "gums" consist largely of starch and dextrin. The syrup should contain at least 70% total sugars, not more than 5% starch and gums, and not more than 3% mineral matter.

Maple.—Canadian maple syrup is legally defined as made by the evaporation of maple sap, and containing not more than 35% of water. The dry substance should meet all the standards for maple sugar.

INVERT SYRUP.

In 1916, more than two million gallons of invert sugar syrups was used in the United States. Jordan and Chesley[48] give the following compositions:—The "light syrup" is made from refined sugar, and contains from 70 to 78% invert sugar, and from 0.5 to 4% of unchanged sucrose. Some brands contain up to 33% sucrose. "Dark syrup" is made from raw sugars, or mixtures of (1) invert from raw sugar and molasses; (2) "light syrup" and molasses; or (3) invert with soured honeys and sugar-house wastes. The "dark syrup" rarely contains more than 72·5% total sugars, a varying amount of which (18 to 73%) is invert sugar. The ash varies from 0·5 to 3·5%.

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[45] *Agric. J. India*, 1917, **12**, 442; *J.*, 1917, 1022.

[46] *J. Ind. Eng. Chem.*, 1917, **9**, 492; *J.*, 1917, 662.

[47] *J. Ind. Eng. Chem.*, 1917, **9**, 750; *J.*, 1917, 1058.

[48] *Loc. cit.*

The invert syrup "Nulomoline"[49] is a substitute for glycerin for purposes in which a non-drying and softening material is required. It contains about 81% of invert sugar, 18% water, and only traces of sucrose and ash. It is manufactured by boiling an aqueous solution of refined cane sugar with a small quantity of citric acid and bleached gum arabic, in a steam-jacketed pan until the boiling point reaches 232·5° F. Steam is then turned off, and cold water added to the syrup to check the boiling. The hot syrup is then rapidly cooled by flowing over metal plates, between which cold water is circulated.

OTHER SUGARS.

Glucose.—Instead of treating starchy material in bulk with acid, Rudman[50] allows a spray of acid to react with the starch in the form of dust, by forcing the starch and acid through suitable nozzles into a closed vessel. The air entering the nozzles may be previously heated. The same effect may also be obtained by passing the starch through a vibrating screen, or down a vibrating chute, and the acid sprayed upon it during its fall.

A continuous type of starch converting apparatus is patented by Sovereign and Lenders[51], the converted syrup being discharged at one end of the apparatus, proportional to the quantity of acidified starch entering at the other end. The advantage of this system consists in the uniform composition of the product.

It has been proposed[52] to employ *Mucor Boulard, No. 5* for saccharification of starch. To obtain a product rich in glucose and containing little maltose and dextrins, the starchy material is heated under pressure with dilute acid, transferred to a closed vat, and seeded with the mould at 40° C. Air is then blown through the liquid. The treated liquid is concentrated and yields a colourless syrup, without treatment with charcoal. Products containing a high percentage of dextrins are prepared by employing certain acids in the preliminary digestion, and also by aerating more strongly during saccharification.

In studying muta-rotation of glucose, Hudson and Dale[53] prepared pure samples of α and β glucose by hydrolysis of maize starch, and crystallisation from solution containing acetic acid At ordinary temperatures, and with low acidity, the α-glucose predominates. At a higher temperature, and in the presence of more acetic acid, the β-glucose separates. After recrystallising, the α-glucose gave an initial rotation of +110° and the β-glucose an initial rotation of +90 6°

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[49] U.S. Pat. 1181086 (1916); *J.*, 1916, 648.

[50] Eng. Pat. 16362 (1914); *J.*, 1915, 882.

[51] U.S. Pat. 1183408 (1916); *J.*, 1916, 759.

[52] Fr. Pats. 475791 and 477927 (1914); *J.*, 1916, 64, 1170.

[53] *J. Amer. Chem. Soc.*, 1917, **39**, 320; *J.*, 1917, 346.

The following modification of Behrend's method of preparing pure β-glucose is proposed by Mangam and Acree.[54] α-Dextrose is dissolved completely in boiling pyridine (25 grms in 25 c.c) and the solution allowed to crystallise for twenty-four hours in an ice-box. β-Dextrose separates with one molecule of pyridine, which it loses readily in the air, *in vacuo* over sulphuric acid, or in an oven at 120° C. When the pyridine is completely removed, the product shows an initial rotatory power of 20° to 25°. The yield is 70 to 85 %.

Lactose -In the manufacture of lactose from whey, Dietrich[55] heats the whey under pressure, in the absence of air, to coagulate the non-sugar. The liquid is then cooled, filtered, and concentrated to a syrup *in vacuo*, and finally pasteurised in hermetically closed vessels.

Lævulose. A method of producing lævulose from plants containing inulin is described by Cartier Saint-René.[56] The pulped material is treated with acid, or a suitable ferment, to convert the inulin into lævulose. An excess of lime is added to precipitate, calcium lævulosate, which is separated by filter-pressing, and washed with water It is then decomposed by carbonic, sulphuric, or sulphurous acids, the insoluble lime compound filtered off, and the filtered liquid concentrated and crystallised

Analyses of juices from twenty varieties of apples by Eoff[57] gave the following results Juice from fifteen varieties of American apples contained from 7·9 to 12 total sugars, including 7·6 to 31·2 % sucrose, 52·5 to 71·7 lævulose, and 5 to 37 6 dextrose. Juices from five varieties of French apples contained from 9 1 to 13·8 % total sugars, including 2·1 to 29 5 sucrose, 58 2 to 74·2 lævulose, and 12·3 to 23·7 dextrose In every instance the amount of lævulose exceeded the combined amounts of sucrose and dextrose.

Maltose -Kaufmann[58] proposes to extract malt and separate the aqueous solution. The residue is treated with more water, cassava starch added, and the mixture (sp. gr. 1·16) is kept at 60° to 70° C. for

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[54] *J Amer Chem Soc*, 1917, **39**, 965; *J*, 1917, 730.

[55] U S Pat 1201627 (1916), *J*, 1916, 1229

[56] Fr. Pat 474015 (1913), *J*, 1915, 727

[57] *J Ind Eng Chem*, 1917, **9**, 587, *J*, 1917, 903.

[58] U.S Pat 1181460 (1916); *J*., 1916, 703

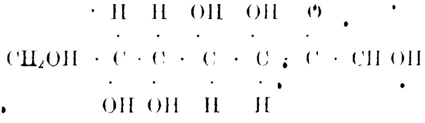
30 minutes. After boiling and cooling to 60° C., the aqueous malt extract is added, reducing the density to about 1·125, and the mixture is kept at 60° to 65° C. until saccharification is complete, after which it is filter-pressed.

Mannose.—Hudson and Sawyer[59] have prepared the pure sugar from seeds of the tagua palm (*Phytelephas macrocarpa*), by hydrolysis with sulphuric acid.

Melibiose.—Hudson and Harding[60] ferment pure raffinose with bakers' yeast at ordinary temperatures. After fermentation is complete (thirty-six to forty-eight hours), a slight excess of basic lead acetate is added and the liquid filtered. In the filtrate, the excess of lead is precipitated by hydrogen sulphide, and the excess of hydrogen sulphide removed from the filtrate by a current of air. The liquid is concentrated to a syrup *in vacuo*, 95% alcohol added, and finally a few crystals of pure melibiose to induce crystallisation.

Xylose is prepared from cottonseed husks by the following method of Hudson and Harding.[61] The material is steeped in dilute ammonia, boiled with dilute sulphuric acid to hydrolyse the xylan, neutralised with lime, separated from calcium sulphate, acidified with phosphoric acid, decolourised, concentrated, and crystallised with the aid of alcohol.

New Sugars.—La Forge[62] isolated 50 grams of a new sugar, *d*-mannoketoheptose from 3·5 kilos of pulped Avocado or Alligator pear (*Persea gratissima*). This is the first heptose isolated from a natural source. It melts at 152° C. without decomposition, is not fermentable, specific rotatory power $\left[\alpha\right]_D^{20}$ = about + 29° in aqueous solution. The *p*-bromophenylhydrazone melts at 179° C., and the phenylosazone at 200° C. Its configuration is :



$$\begin{array}{ccccccccccccc} & & H & & H & & OH & & OH & & O & & \\ & & \cdot & & \cdot & & \cdot & & \cdot & & \cdot & & \\ CH_2OH & \cdot & C & \cdot & C & \cdot & C & \cdot & C & \cdot & C & \cdot & CH_2OH \\ & & \cdot & & \cdot & & \cdot & & \cdot & & & & \\ & & OH & & OH & & H & & H & & & & \end{array}$$

Another heptose sugar was found by La Forge and Hudson[63] in the leaves and stems of *Sedum spectabile* (one of the stone crops). The sugar itself was not isolated, but crystalline phenyl- and bromophenylosazones (m. pt. 197° and 227° to 228° C., respectively) were prepared and analysed. The heptose is nonfermentable, and is not oxidised by bromine. As it yields two heptitols on reduction, it is regarded as a ketose.

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[59] *J. Amer. Chem. Soc.*, 1917, **39**, 470; *J.*, 1917, 467.
[60] *J. Amer. Chem. Soc.*, 1915, **37**, 2734–2736; *J.*, 1916, 62.
[61] *J. Amer. Chem. Soc.*, 1917, **39**, 1038; *J.*, 1917, 730.
[62] *J. Biol. Chem.*, 1917, **28**, 511; *J.*, 1917, 229.
[63] *J. Biol. Chem.*, 1917, **30**, 61; *J.*, 1917, 731.

ANALYTICAL METHODS.

(A) *Sucrose.*

The Ventzke sugar scale of saccharimeters has hitherto been based on the "conversion factor" of 100 Ventzke = 34·657 absolute rotation, due to the work of Herzfeld and Schonrock. As this factor gives erroneous values for specific rotatory power, the Ventzke scale is only approximately true. The subject has recently been studied by Bates and Jackson,[64] of the U.S. Bureau of Standards, by measuring the rotations of solutions of pure sucrose, first on a polarimeter with monochromatic light, and again on various types of quartz-wedge saccharimeters with white light. Two sources of monochromatic light were used, namely, sodium vapour (λ = 5892·5° A.) and mercury vapour (λ = 5461° A.). The mean value of ten experiments gave the following results: (1) A normal sucrose solution (26·0 grams in 100 c.c. metric) gave absolute rotations, at 20° C., of 34·617° (λ = 5892·5° A.) and 40·763° (λ = 5461° A.). (2) The same normal solution gave a saccharimeter reading of 99·89° S. on the Herzfeld-Schönrock scale. (3) The conversion factors for the two monochromatic light sources are: 100° sugar scale = 34·620° (λ = 5892·5° A.), and 40·690° (λ = 5461° A.) at 20° C., as compared with 34·657 (λ = 5892·5° A) by the Herzfeld-Schonrock factor. (4) The difference between the absolute rotations of the normal quartz plate, and the normal sugar solution is 0·003° for λ = 5892·5° A., and 0·073° for λ = 5461° A. (5) The difference in rotation in sugar degrees (calculated from absolute rotations of the normal sugar solution on the saccharimeter) for the two monochromatic light sources was

Reading (λ = 5461° A.) − Reading (λ = 5892·5° A) = 0·19° S.

(6) The specific rotation of sucrose (calculated from the absolute rotations of the normal solution) for the two monochromatic light sources were: $[\alpha]^{20}_{\lambda = 5892\cdot5°\,A} = 66\cdot529$; $[\alpha]^{20}_{\lambda = 5461\,A} = 78\cdot342°$. (7) The agreement between the accepted value, 66·502° and the above value 66·529 for sodium light, is in contrast to the disagreement between 66·502° and 66·627° based on the Herzfeld-Schönrock conversion factor, thus corroborating the new conversion factor 34·620° (λ = 5892·5 A). (8) The calculated thickness of the normal quartz plate gives 1·5934 to 1·5940 mm.

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[64] *U.S. Bureau of Standards*, Bull. No. 268, 1916; *see J.*, 1916, 1126.

In the determination of sucrose by Clerget's method, the accuracy of the Herzfeld factor, 142·66, has been questioned by several chemists. Stanek finds possible differences of 0·1 in the constants obtained by reading more or less promptly after inversion. Koydl has found variations from 142·29 to 142·99. Walker proposes 142·92, based on experiments with pure sucrose. Pellet[65] adopts 142·96 for a particular saccharimeter, and points out that the constant should be determined for each saccharimeter used. He states that the constant may vary from 142·66 to 143·00 according to the time which elapses between inversion and polarisation, owing to mutarotation of the inverted solution. The constant 142·66 is only applicable when the inverted solution is cooled rapidly, and the reading taken in less than thirty minutes after inversion. Beyond this period, the constant varies from 142·87 to 142·95.

C. A. Browne[66] recommends the following modification of the Herzfeld formula, in order to correct for change of rotation with change of concentration:

$$S = \frac{100\,(A-B)}{142\cdot66 - t/2 - 0\cdot0065\,[142\cdot66 - t/2 - (A-B)]}$$

When $t = 20°$ C., this reduces to:

$$S = \frac{100\,(A-B)}{132\cdot66 - 0\cdot0065\,[132\cdot66 - (A-B)]}$$

He recommends inversion by means of invertase as a valuable control on the accuracy of the more rapid method of acid inversion.

Instead of heating the sucrose with acid for a definite time, and at a definite temperature, Walker[67] simplifies the process by heating the sugar solution to an approximate temperature, then adding the acid, and allowing inversion to take place during cooling. Experiments with pure sucrose solutions and with molasses gave uniform results when the acid was added to the solution previously heated to any temperature between 70° and 63° C., and then left to cool for fifteen minutes or longer. Thus, an approximate temperature of 67° C. may be adopted when adding the acid, and no further regulation of temperature is necessary. The cooling for 15 minutes in air, and finally in cold water, completes the inversion. The method agrees closely with that of Herzfeld, using the same factor, 142·66—0·5*t*.

An important paper on "The use of enzymes and special yeasts in carbohydrate analysis," by W. A. Davis[68] should be noticed. For the estimation of sucrose, he employs invertase prepared from bottom yeast by treatment with toluene at 25° to 30° C. for a fortnight. The invertase, thus prepared, is free from maltase and zymase, and can be kept for several years. Inversion of a sugar solution is effected by incubating for 21 hours at 38° C., with 1 c.c. of the invertase and a few drops of toluene. The sucrose present is calculated by means of Herzfeld's table of constants. It is not necessary to apply any correction for the slight optical activity of the invertase added, as the error is inappreciable.

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[65] *Int. Sugar J.*, 1915, **17**, 558–560; *J.*, 1916, 134.

[66] *J. Assoc. Offic. Agric. Chem.*, 1916, **2**, No. 3, 134; *J.*, 1917, 153.

[67] *Int. Sugar J.*, 1917, 31; *J.*, 1917, 153.

In order to shorten the time required for hydrolysis, when using yeast at 55° C., Pellet[69] employs yeast liquefied by 7 % of sodium salicylate, thus reducing the time from about 1½ hours to 20 or 30 minutes, under definite conditions of concentration.

Numerous reagents have been proposed for destroying reducing sugars in order to determine sucrose by direct polarization. These include potassium and sodium hydroxides, by Dubrunfaut; baryta and strontia, and hydrogen peroxide in conjunction with sodium hydroxide, as suggested by Pellet and Lemeland, and Vollant. Muller[70] employs an alkaline solution of bismuth subnitrate containing Rochelle salt.

For the determination of minute percentages of sucrose, Pellet and Geslers[71] modify the α-naphthol test by shaking the solution with the reagent and sulphuric acid in a test-tube, and comparing the depth of colour produced with that of standard solutions, containing from 0·1 to 0·2 grm. sucrose per litre.

Blake[72] for the same purpose, prepares a series of standard tints by mixing solution of cobalt nitrate and copper sulphate, corresponding to the tints given by solutions containing up to 20 parts of sucrose per million. For larger proportions of sugar, he employs mixtures of red and blue organic dyes.

(b) *Other Sugars.*

Aldoses.—Bougault[73] proposes oxidation by iodine in the presence of sodium carbonate, in accordance with the equation:—$R{\cdot}CHO + H_2O + I_2 = R{\cdot}COOH + 2HI$. The estimation is effected by adding an excess of iodine, and titrating samples of the solution at regular intervals until the loss of iodine reaches a low constant value within half an hour (90 minutes in the case of mannose).

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[68] *J.*, 1916, 202.

[69] *Bull. Assoc. Chim. Sucr.*, 1915, **33**, 29, 36, 39; *J.*, 1916, 320.

[70] *Int. Sugar J.*, 1916, 274–275; *J.*, 1916, 858.

[71] *Sucr. Indig.*, 1896, **48**, 87.

[72] *Int. Sugar J.*, 1917, **19**, 26; *J.*, 1917, 152.

[73] *Comptes rend.*, 1917, **164**, 1008; *J.*, 1917, 899.

Hexoses.—Bertrand and Duchaček[74] have shown that the Bulgarian bacillus (*Bacillus acidi lactici Massol*) converts hexoses into lactic acid, but acts upon only one of the disaccharides, namely lactose. Margaillan employs this organism for separating lactose and glucose from sucrose.

Galactose.—For detecting *d*-galactose in the presence of other monosaccharides Van der Haar[75] employs *o*-tolylhydrazine. The *o*-tolylhydrazone thus obtained forms colourless needles, m. pt. 176° C. It is practically insoluble in cold water, slightly soluble in cold alcohol, more soluble in hot water or hot alcohol, and easily soluble in pyridine. 100 mgrms. of *d*-galactose can be detected in the presence of a mixture of 50 mgrms. each of arabinose, xylose, rhamnose, dextrose, mannose, and levulose, since none of these forms an *o*-tolylhydrazone.

Von Braun[76] employs benzoyldihydromethylketol-hydrazine. With galactose this reagent forms a colourless crystalline precipitate in from ½ to 2 hours, according to the concentration. Dextrose, levulose, mannose, arabinose, and xylose give no precipitate.

Glucose.—Jackson[77] has determined the normal weight and specific rotatory power of pure glucose, adopting the conversion factor of 34°.620 for the true Ventzke scale (*see* p. 392). A rotation of 100° Ventzke is given by 32·231 grms. of glucose in 100 c.c. The old normal weight of 32·261 grms. is based on the erroneous conversion factor of 34°·657. The specific rotation of glucose is given by the formula: $[\alpha]^{20^\circ C}_{5461} = 62·032 + 0·01257\,C$, where C = grms. of anhydrous glucose weighed *in vacuo* in 100 c.c. Or by $[\alpha]^{20^\circ C}_{5461} = 62·032 + 0·0122\,p + 0·0001897\,p^2$; where p = percentage by weight *in vacuo*.

Glutose.—This non-fermentable sugar occurs in cane molasses. It is determined by H. Pellet[78] by diluting molasses ten-fold, slightly acidifying, and fermenting with bottom-yeast for three days. The reducing power of the residual glutose is then determined by heating with Fehling's solution at 63° to 65° C. for thirty minutes after preliminary clarification with normal lead acetate. Pellet found from 2·6 to 5 % glutose in cane molasses.

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[74] *Ann. Inst. Pasteur*, 1906, **20**, 977.

[75] *Rec. Trav. Chim. Pays-Bas*, 1917, **37**, 108; *J.*, 1917, 1022.

[76] *Ber.*, 1916, **49**, 1266—1268; *J.*, 1916, 1020.

[77] *J. Wash. Acad. Sci.*, 1916, **6**, 530-531; *J.*, 1916, 1126.

[78] *Ann. Chim. Analyt.*, 1917, **22**, 43; *J.*, 1917, 467.

Lactose.—Baker and Hulton[79] determine lactose in the presence of other sugars by utilising the fact that lactose is not fermented by ordinary yeasts. They consider this method preferable to polarimetric methods.

Maltose.—The determination of maltose in the presence of sucrose, or fructose, or both, has been worked out by Davis and Daish.[80] Their method is based on the fact that certain yeasts completely ferment glucose, fructose, and sucrose, without acting upon maltose, which can thus be determined from the final reducing power. The yeasts employed are, *Saccharomyces marxianus*, *S. exiguus*, and *S. anomalus*.

Raffinose.—H. Pellet[81] claims that the determination of this sugar in the presence of sucrose, by the Herzfeld-raffinose formula, is vitiated, by the presence of other optically active substances, even when these remain unaffected during inversion.

Kluyver[82] employs special yeasts for estimating raffinose in complex mixtures of sugars and measures the volume of carbon dioxide evolved by the action of the yeasts, in a specially designed eudiometer. He shows that top-yeasts, (*Torula dattila*, *Schizosaccharomyces Pombe*), and a lactose yeast, all decompose raffinose only to the stage of melibiose and lævulose, the latter of which is fermented, giving carbon dioxide. Bottom-yeast ferments raffinose completely. From the difference between the CO_2 evolved by the action of top- and bottom-yeasts the quantity of raffinose present can be calculated. Biochemical methods have been applied by Kluyver to the analysis of food materials, such as jams, starch-syrups, and in other cases of technical importance.

Hudson and Harding,[83] employ enzymes prepared from top- and bottom-yeasts for determining raffinose in sugar mixtures. Autolysed top-yeast decomposes raffinose as in equation (1) :—

(1) Raffinose Melibiose + fructose

Autolysed bottom-yeast further decomposes melibiose :—

(2) Melibiose galactose + glucose.

The difference in rotation between (1) and (2) is a measure of the raffinose present. Mixtures of 1·5 % of raffinose with sucrose, glucose, fructose, invert sugar, lactose, maltose, cellose, and trehalose, gave results varying from 1·43 to 1·53 % raffinose.

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[79] *Analyst*, 1910, **35**, 512; *J.*, 1911, 43.

[80] *J. Agric. Sci.*, 1913, **5**, 153; *J.*, 1913, 1024, 1025.

[81] *Bull. Assoc. Chim. Sucr.*, 1916, **35**, 112; *J.*, 1917, 935.

[82] *Biochem. Suikerbepalingen*, 1914.

[83] *J. Amer. Chem. Soc.*, 1915, **37**, 2193; *J.*, 1915, 1095.

(c) *Mixtures of Sugars.*

Wilson and Atkins[84] prove that dextrose and maltose are quantitatively oxidised by bromine at ordinary temperatures, whereas levulose is only very slightly oxidised. Hence, a mixture of sucrose, maltose, dextrose, and levulose may be analysed as follows The sucrose is determined by polarization and reduction, before and after inversion by invertase The resulting mixture of reducing sugars is treated with bromine under standard conditions of acidity and temperature for a given time. The final reducing power is due to levulose only, from which is deducted that portion derived from the sucrose On subtracting the calculated rotation, due to sucrose and levulose, from the initial rotation, the rotation due to maltose and dextrose is obtained Similarly, by subtracting the reduction due to levulose only, from the initial reduction, the reduction due to maltose and dextrose is obtained The percentages of maltose and dextrose can then be calculated The oxidation method affords an easy means of detecting abnormal quantities of dextrose in honey, jams, etc

The composition of starch syrup has been studied by Wesener and Teller,[85] who calculate the proportions of maltose and dextrose from the cupric reducing power, and yield of carbon dioxide on fermentation Two samples gave 11·7 and 17·2 dextrose and 22·9 and 16·1 maltose. There were also present reducing substances which ferment with difficulty amounting to about 11 calculated as maltose, or 8 calculated as dextrose, and unfermentable dextrins amounting to about 17

(d) *Copper-reduction methods*

Meade and Harris[86] find that the Meissl-Hiller method gives results 4 to 5% higher when the excess of lead is precipitated as oxalate, than when a carbonate or sulphate is used. Further, that the results are about 5% higher when weighed as cuprous oxide, than when ignited to cupric oxide. The latter agrees closely with the iodometric determination of the copper.

Frerichs and Mannheim[87] prefer Rupp and Lehmann's iodometric method to the Fehling-Soxhlet method, and find that the products of oxidation of the sugar have no action on iodine The authors have recalculated the table published by Rupp and Lehmann

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[84] *Biochem J*, 1916, **10**, 504; *Analyst*, 1917, **42**, 12, *J*, 1917, 154

[85] *J. Ind. Eng Chem*, 1916, **8**, 1009; *J*, 1916, 1229

[86] *J. Ind. Eng Chem*, 1916, **8**, 504; *J*, 1916, 750

[87] *Arch. Pharm*, 1916, **254**, 138, *J*, 1917, 1022

Wedderburn's modification of the gravimetric method[88] consists in reducing the cuprous oxide, in a silica Gooch crucible, by means of alcohol vapour, and the results agree closely with the electrolytic method of reduction. The former method is more suitable for routine work. A solution of the material is clarified with neutral lead acetate, and the excess of lead removed by potassium oxalate.

For determining very small percentages of reducing sugars in the presence of sucrose (high-grade and refined sugars), Pellet[89] employs a Fehling solution containing only 60 grms. of sodium hydroxide per litre of mixed solutions. 20 c.c. of this copper solution, 20 c.c. of the sugar solution to be tested (containing less than 0·10 grm. of reducing sugar) and 10 c.c. of water are heated to 60-62° C. for 16 minutes, and the precipitated cuprous oxide filtered off, after diluting with 50 c.c. cold water, heated in a muffle furnace, and weighed as cupric oxide. For rapid work, the cuprous oxide is collected on a small disc of filter paper of definite area, and the depth of the red colour compared with a series of similar discs, prepared from known quantities of a standard invert sugar solution (1 c.c. = 0·005 grm.), treated in the same manner.

Maquenne[90] also discusses methods for the determination of small quantities of reducing sugars in presence of sucrose, by heating the reaction mixture at a definite temperature, and for a definite time. The reduction due to sucrose can be minimized, but not entirely eliminated, by heating between 65° and 75° C. for 10 minutes or longer. Slight fluctuations of temperature do not affect the results appreciably.

(e) *Miscellaneous.*

The calcium carbide method of estimating water has already been applied to coal, tea, coffee, cocoa, butter, cordite, wool, and other substances which readily oxidise on heating. The method was first suggested by Danne, in 1900, since when special apparatus has been designed by Dupré,[91] Roberts and Fraser,[92] Cripps and Brown,[93] Masson,[94] and Campbell.[95] West[96] has designed an apparatus in which the acetylene evolved from saccharine materials containing water, is measured in a gas burette

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[88] *J. Ind. Eng. Chem.*, 1915, **7**, 610; *J.*, 1915, 854.

[89] *Bull. Assoc. Chim. Sucr.*, 1913, **31**, 183; *J.*, 1914, 35.

[90] *Comptes rend.*, 1916, **162**, 207; *J.*, 1916, 320.

[91] *Analyst*, 1906, **31**, 213; *J.*, 1906, 780.

[92] *J.*, 1910, 197.

[93] *Analyst*, 1909, **34**, 519; *J.*, 1910, 43.

[94] *J. Chem. Soc.*, 1910, **98**, 851; *Chem. News*, 1911, **103**, 37; *J.*, 1910, 216; 1911, 157.

[95] *J.*, 1913, 67.

[96] *J. Ind. Eng. Chem.*, 1916, **8**, 31; *J.*, 1916, 554.

Snell[97] gives results of his electrical resistance test on maple syrups, and mixtures of maple and sucrose syrups as influenced by the addition of basic lead acetate A graph is plotted, with volumes of lead acetate solution as abscissae, and resistances as ordinates The abscissa of the point of intersection of two straight lines, forming the graph is called the "lead number", and ranged from 1·9 to 6·6 with 70 genuine maple syrups. Of 20 syrups containing 30 of sucrose syrup, 17 gave smooth curves. Of 20 syrups containing 10 of sucrose syrup, 18 gave smooth curves, and the remaining two gave points of intersection outside the limits for genuine syrup

In the analysis of saturation scums, Stanek[98] determines the total carbon by oxidation with chromic and sulphuric acids and weighing the carbon dioxide evolved. The sugar content is determined in a separate portion. The quantity of carbon dioxide due to sugar is deducted from the total found, and the balance calculated to carbon percentage in organic non-sugars

PART 2 —STARCHES

(a) SOURCES

According to Goris,[99] the horse chestnut kernel contains 2 to 3 fat, 6 to 7 nitrogenous matter, and 20 to 30 starch. Owing to the presence of saponins, the pulp or flour cannot be used as foodstuff without treatment to remove them He recommends washing with a 0 1 solution of hydrochloric acid. The starch thus treated is white, odourless and tasteless and might serve as food or for the production of alcohol. Factories for the production of starch from horse-chestnuts were formerly erected near Paris but were not remunerative, owing to the cost of labour and transport

(b) MANUFACTURE.

Goldbeck[100] describes a method of wheat-starch manufacture giving a yield of 57–60 of starch, as compared with 31–52 by the old methods. The new method is due to the more perfect separation of the starch from the gluten by the following operations The flour is kneaded into a dough with water, and washed in an extractor. The starch-milk, thus obtained, is passed through the usual sieves, and the fine starch separated by centrifugal action. The starch, remaining on the sieves, is separated from the admixed gluten by allowing the gluten to ferment, or by treating it with dilute ammonia and acetic acid, and centrifuging the mixture. The gluten and bran thus separated may be used as feeding stuffs.

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[97] *J Ind Eng Chem*, 1916, **8**, 241 *J*, 1916, 182

[98] *Z Zuckerind Bohm*, 1916, **40**, 201, *J*, 1916, 701

[99] *Comptes rend*, 1917, **165**, 345, *J*, 1917, 1107

[100] *Chem -Zeit*, 1916, **40**, 829-830, *J*, 1916, 1169

The manufacture of a granular form of starch is patented by Bauer.[101] Starch is mixed with a binding material ("mazam," a dextrin of high molecular weight) in liquid form, and the mixture is dried in a current of air without gelatinization of the starch. The product consists of hard pellets which break down in water at ordinary temperatures, forming a milky liquid without residue.

The method of purifying waste water from potato-starch factories in Hungary is thus described by Halm.[102] The volume of waste waters varies from 1·4 to 2·8 cubic ft. per cwt. of potatoes, representing a daily discharge of from 159,121 to 918,212 cubic ft. of waste water. Purification by irrigation was found too cumbersome, and good results were obtained on the following principles:—Purification of the innocuous water, derived from potato-washing, by subsidation in a tank capable of holding the deposited solid matters collected during the whole season's working. This deposit generally amounts to 5 of the potatoes worked, *i.e.*, about 25 cubic ft. per 10 ton wagon of potatoes. The noxious waters from the starch manufacture, amounting to two-thirds of the whole, are run over dyked areas of ground to a depth of about 3 feet, and then left to ferment. The area required for small factories is about 5 acres, and for large factories 85 acres. Part of the water disappears by percolation and evaporation; the remainder requires about 4 months for fermentation. The soil thus manured is suitable for cultivation.

(c) ANALYSIS.

Von Fellenberg[103] employs a direct method of estimating starch, based on the solubility of starch in a 50 calcium chloride solution, its precipitation by iodine, and the decomposition of this precipitate by alcohol.

Davis[104] proposes a method based on the use of taka-diastase, prepared from *Aspergillus oryzæ*, which quantitatively converts starch into a mixture of two sugars only—maltose and dextrose, which can then be determined by rotation or by reducing power. The material is first freed from sugars by extraction with boiling 80 alcohol in a Soxhlet extractor, also, if necessary, extracted with cold water to remove gums, amylans, etc. A weighed portion, 2 grms., is then gelatinized with 200 c.c. of water in a 250 c.c. beaker-flask heated for ½ hour in a water-bath at 100 ° C. The solution is cooled to 38° C., and 0·1 grm. of taka-diastase added, also 2 c.c. of toluene; the mixture is then left for 24 hours for conversion to take place. It is then heated in a boiling water-bath to destroy the diastase, and the clear portion filtered through a fluted filter-paper into a 500 c.c. measure flask. The residue is washed several times by decantation until the volume in flask amounts to 175 c.c. The necessary quantity of basic lead acetate is added to precipitate tannins, etc., the volume required varying from 5 to 25 c.c. (a large excess of lead should be avoided.) When the precipitation is complete, the solution is made up to 500 c.c. and filtered. 100 c.c. of the filtrate is placed in a 110 c.c. flask, the slight excess of lead precipitated by sodium carbonate, and the volume adjusted to 110 c.c. at 15° C. 50 c.c. of the filtrate from the lead carbonate is used for the reduction, and another portion polarized in a 400 mm. tube.

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[101] U.S. Pats. 1175113 and 1175114 (1916); *J.*, 1916, 482.

[102] *Vizugyi Kozlemenyek*, 1916, **6**, 1; *J.*, 1916, 1126.

[103] *Mitt. Lebensmittelunters. Hyg.*, 1916, **7**, 369; *J.*, 1917, 935.

[104] *J.*, 1916, 207.

A polarimetric method of determining starch, in the presence of other optically active substances, is suggested by Baumann and Grossfeld.[105] It is based on the complete precipitation of starch by lead tannate, when the latter is formed in the solution. The difference in rotations of the same solution, with and without the precipitation of the starch, multiplied by 5·111, gives the percentage of starch present, this factor being calculated from the average rotatory power (+ 183·7) of various starches. The error of the method does not exceed 0·2%, with substances containing from 10 to 60 of starch, together with large proportions of sucrose, dextrins, etc.

For detecting potato starch in flour, Blunck[106] employs "metachrome red G Agfa." Potato starch and cell tissues are coloured a bright golden yellow by this reagent, whereas cereal starches are unaffected.

For the determination of starch in raw potatoes, Ewers[107] heats the ground sample with dilute hydrochloric acid. After cooling, the solution is treated with sodium molybdate solution, diluted to known volume, filtered, and polarised. The reading in Ventzke degrees × 0·44007 = percentage of starch.

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[105] *Z. Unters. Nahr. Genussm.*, 1917, **33**, 97; *J.*, 1917, 662.

[106] *Z. Unters. Nahr. Genussm.*, 1915, **29**, 246; *J.*, 1916, 1077.

[107] *Z. offentl. Chem.*, 1915, **21**, 232; *J.*, 1916, 432.

The most accurate value for starch in potato is found by subtracting from 100 the sum of the percentage of moisture, ash, cellulose, ether-extract, proteins, and pentosans. Values so obtained are higher than those given by the Baumert-Bode method and Ewers' polarimetric method. The values deduced from specific gravity, from the table of Behrend, Märcker, and Morgen, are about 0·5% lower than results by Ewers' method. De Vries[108] has constructed a new table, "Groning's Table," which gives more accurate values.

Wieninger[109] has devised a polarimetric method of determining starch in spent grains, after precipitating the lævorotatory substances by zinc sulphate. The rotation due to non-amylaceous dextrorotatory matters is found by precipitating both the lævorotatory substances and the starch in a second portion of the liquid extract, by means of phosphotungstic acid.

The gelatinizing temperature of starches is determined by Francis and Smith[110] by means of a special thermo-micro-slide, with hot water circulation. The starch to be tested is placed on the slide, covered with water, and the slide heated at the rate of 1° C. per minute. The temperature is noted when the starch granules lose their polarizing power.

Dox and Roark[111] employ a No. 8 electric incubator for the microscope stage. The gelatinization points of the starches from 13 varieties of maize were found to vary from 64·1° to 71·1° C., but concordant results were obtained for each variety.

The viscosity of starch solutions is determined by MacNider[112] in a Scott viscometer, at the boiling point of the starch solution, relative to water, also at boiling point. The starch solution was previously boiled with steam for 1 hour in a model "kettle" of $1\frac{3}{4}$ gallon capacity, similar to the large "kettle" used in the preparation of warp sizing. Various grades of thick-boiling starch (0·5 lb. per gallon water) gave viscosities of from 2·89 to 4·58, whilst thin-boiling starch (1 to 2 lb. per gallon water) gave viscosities of from 1·27 to 2·45. Maize starch (4 lb. per gallon) had a viscosity of 3·54.

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[108] *Chem.-Zeit.*, 1916, **40**, *Rep.* 153.

[109] *Z. Ges. Brauw.*, 1915, **38**, 257; *J.*, 1916, 377.

[110] *J. Ind. Eng. Chem.*, 1916, **8**, 509; *J.*, 1916, 750.

[111] *J. Amer. Chem. Soc.*, 1917, **39**, 742; *J.*, 1917, 560.

[112] *J. Ind. Eng. Chem.*, 1917, **9**, 597; *J.*, 1917, 899.

PART 3. GUMS

(a) SOURCES AND STATISTICS

Montandon[113] states that substitutes for gum arabic are obtained from the following Brazilian plants. Different species of "Angico," *Enterolobium ellipticum* (*Pithecolobium gummiferum*) "Arvore da gomma" or "gomma lagrima" (*Vochysia gummifera*) in the province of Rio de Janeiro, "Vinheiro do Campo" or "Arvore do Vinho" (*Vochysia thyrsoidea*) in the State of Minas Geraes. The best quality, or "gomma lagrima," is colourless and transparent, completely soluble in eleven parts of cold water. A sample had the following composition: Water, 11·79; arabin, 87·67; yellow bitter substance 0·03; resinous substance, 0·01; insoluble matter, 0·012; and ash, 0·44. Consignments of Brazil gum have been exported to Liverpool and to Germany from 1900 onwards.

The various species of *Astragalus* from which gum-tragacanth is obtained, grow on the mountains surrounding the Persian plain. The price of the gum[114] has increased 5 to 10% since the outbreak of war. The present prices are as follows: First grade, 3s. per lb.; second grade, 1s. 8d.; third grade, 1s. 2d.; fourth grade, 10d.; and fifth grade 6d. The principal Persian markets are Hamadan, Shiraz, Kerman, and Kermanshah. From 150 to 200 tons is exported annually from Hamadan. Before August, 1914, half of this amount was shipped to Russia, and the other half to America and Great Britain. Great Britain and Russia are the largest importers of Persian gum-tragacanth, followed by Turkey, India, and the United States. The exports in 1913-14 were valued at £233,000.

ANALYSIS.

For the determination of gum in French officinal syrups, Luce[115] recommends the method of Rocques and Sellier. The syrup is diluted five-fold, and 25 c.c. treated with 50 c.c. of 95% alcohol, and 2 c.c. of saturated alcoholic lead acetate solution. Bellier's method, though not so accurate, is sufficiently so for most purposes. 20 c.c. of five-fold diluted syrup is treated with 40 c.c. of 95% alcohol, and 1 c.c. of 10%

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[113] *Chacaras e Quintaes*, 1916, **13**, 417; *J.*, 1917, 155.

[114] *U.S. Comm. Rep.*, No. 293, Dec. 15, 1915; *J.*, 1916, 134.

[115] *J. Pharm. Chim.*, 1916, **14**, 13-19.

aqueous solution of calcium chloride. After 24 hours, the precipitate is washed by decantation with 60 c.c. of 65 % alcohol in three portions; transferred to a tared filter, again washed with 20 c.c. of 65 % alcohol, dried for 6 hours, and weighed. Since the moisture content of gum is about 12 %, the weight is multiplied by 100 ÷ 88. These methods are not applicable to gums containing dextrins.

Waters and Tuttle[118] recommend basic lead acetate as the most distinctive reaction. Mixtures of neutral ferric chloride and alcohol, and of copper sulphate and sodium hydroxide, are valuable as confirmatory agents. For quantitative determination, they employ a solution containing 50 grms. copper acetate, ammonia in excess, and 50 % of alcohol in 1 litre.

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[118] *U.S. Bureau of Standards, Technol. Paper*, No. 67; *J. Franklin Inst.*, 1916, **181**, 266; *J.*, 1916, 375.

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FERMENTATION INDUSTRIES.

By Arthur R. Ling,

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Owing to the continuance of the war, it has been found necessary to restrict considerably the production of potable fermented liquors. It might, therefore, have been anticipated that the research work connected with the production of these liquors would have undergone a corresponding diminution. And this would undoubtedly have been the case had it not been that the restrictions themselves have rendered necessary special investigations to meet their demands; as it is, these latter have quite counterbalanced any deficiency in what may be termed the routine investigations of normal times. Activity in this direction is particularly noticeable in Germany and in Austria, more especially in the former country, where the most drastic changes have had to be made both in regard to materials employed and methods adopted in the production of beer, on account of the shortage of grain. It has been deemed expedient to deal as fully as space would permit with the investigations on which these changes have been based, since they are, to say the least, suggestive so far as our home production is concerned. In most other branches of fermentation technology, however, there has been a distinct falling off in the number of papers published, which may to some extent be accounted for by the fact that it is undesirable at the present time to publish some of the facts which have been ascertained in regard to fermentation products. Contributions of an academic character have been well maintained both in quantity and quality; and although there are no striking discoveries to place on record, attention is called to a considerable number of valuable papers in this category.

CHEMISTRY.

The greater part of the investigations in pure chemistry which concern the fermentation industries during the period under review are, as usual, those which describe the actions of different enzymes.

In order to prevent confusion, the writer has adopted in this section wherever possible the nomenclature for enzymes which connotes the particular substrate on which they act, thus amylase instead of diastase, sucrase instead of invertase. Following H. E. Armstrong, he has also adopted the terms amyloclastic and proteoclastic instead of amylolytic, proteolytic.

Starch Hydrolysis.—In his fifty years' retrospect of brewing science[1] H. T. Brown remarked that the "starch question" had its birth in 1811 when Kirchhof observed that starch under the influence of "vegetable albumin" of grain yields a crystallisable sugar. Yet so difficult and complex is the subject of starch hydrolysis that he ventured to predict that chemists will not be united on it even in its bicentenary, 2011 A.D. The writer believes that one of the chief factors which has operated in keeping back definite conclusions on this subject is that starch has been regarded as a chemical entity in the same sense as if it were a crystalline compound. Chemists have been in the habit of speaking of the starch molecule, whereas if there be any meaning whatever in the term it is to be regarded in a physiological rather than in a chemical sense. It is true that Brown and his colleagues were among those who recognised that there is a difference in the behaviour of different starches towards malt amylase, and this has been amply confirmed by subsequent work. Much good and useful work has been carried out, and certain definite products have been isolated, yet the writer ventures to think that it has not been sufficiently recognised that the substrate most frequently employed in experiments on the hydrolysis of starch by malt amylase, *e.g.*, potato-starch paste, is of a mixed nature, so that in all probability several reactions are proceeding at the same time. Against this it may be urged that in some cases soluble starch prepared by the Lintner method has been employed, but even so we are by no means sure that we are dealing with a single chemical substance. Then again the multiple nature of malt amylase has not been sufficiently recognised until comparatively recent times.[2] Among the compounds which have been isolated as products of the action of malt amylase on starch, maltose stands out as a statical unit, and in all probability we must place in the same category the so-called iso-maltose, although this has not hitherto been obtained in a crystalline state. The writer must, however, in this case associate himself with Syniewski that the iso-maltose has the characteristics of a dextrin. The malto-dextrins, on the other hand—the first member of which to be recognised was described by Herzfeld, its characteristics being more accurately defined later on by Brown and Morris—have not the same claims to be statical compounds as has maltose. It is probable that the whole series exists in a colloidal state, tending more towards the character of definite chemical compounds in the lower members. The conception that these substances exist associated in a kind of solid solution is one which might explain the rule of definite relation between the optical and reducing properties of these hydrolytic products, on which H. T. Brown and his colleagues have so strongly insisted; in a broad sense it is undoubtedly correct.

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[1] *J. Inst. Brewing*, 1916, 22, 293.

[2] Some of the recent work to be recorded in this Report deals with the action of purified amylase on a starch substrate, but interesting as the results are, and whilst admitting that the experiments are based on a sound scientific plan, it would obviously be wrong to compare them with the results of the previous workers who employed malt extract and starch in other forms. Still in the general trend of the reactions may be noted some similarity. One interesting point which recent work seems to indicate is that working with purified enzyme preparations and a more definite substrate the reaction only appears to be linear in the very early stages, the main portion proceeding according to the logarithmic law of unimolecular reactions (cp. p. 409).

The work to which the writer will have to draw attention this year has been carried out with a knowledge of one particular factor, of which the earlier workers to say the most had but a vague notion. This factor is the concentration of H-ions. It is true that it was common knowledge that the results were influenced by the acidity of the medium as determined by titration against indicators, but this is not synonymous with the concentration of H-ions.

B. Viswanath, T. L. Row, and P. A. R. Ayyangar[3] claim to show the influence of certain salts on the liquefaction of starch. Their method of experiment is to shake one gram of rice starch with solutions of the different salts of N/10 concentration at 70° F. for an hour, and subsequently digest the liquid with 15 c.c. of malt-extract for two hours at 30° C. The liquid made up to 100 c.c. is filtered with kaolin and 50 c.c. of the filtrate hydrolysed with hydrochloric acid; the dextrose is then estimated and calculated to starch. The results show the percentage of starch hydrolysed in presence of the substances employed to be as follows:—Distilled water, 11·91 %; caustic potash, 67·51 %; sodium carbonate, 26·62 %; calcium carbonate (suspension), 25·01 %; hydrochloric acid, 23·00 %; sodium sulphate, 22·06 %; magnesium sulphate, 20·40 %; sodium chloride, 19·00 %; calcium chloride, 13·50 %. The authors employed the temperature of 30° C. as on the evidence of Warth and Darabsett[4] there is no appreciable erosion of rice starch granules at that temperature. It should be pointed out that amylolytic activity will be arrested in presence of $N/10$ solutions of caustic potash, sodium carbonate, and hydrochloric acid, whilst the other substances will probably be without action at 30° C. on the diastase.

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[3] *Memoirs Dept. Agric., India*, **4**, [5], 160; *J.*, 1916, 858.

[4] *Ibid.*, 1914, **3**, 135; *J.*, 1914, 433.

The production of glucose by the protracted action of pancreatic amylase and of malt amylase (diastase) on starch is noted by H. Sherman and P. W. Punnett.[5] They argue from the fact that glucose is produced even by the use of highly purified enzyme preparation that it is not to be attributed to the presence of maltase. The writer of this report in several papers on the subject has pointed out that dextrose is one of the products of the protracted action of malt amylase on starch, and from the fact that its production was observed in the case of malt amylase preparations having no action on maltose, he concluded that it was *not* to be attributed to the presence of maltase. Finally, production of glucose under these conditions has been noted by numerous other observers.[6]

Between the years 1901 and 1906 several papers were published by Maquenne and Roux in which the view is put forward that starch granules consist of a mixture of amylose and amylopectin. The existence of these substances, although by no means established, is accepted by some. H. C. Sherman and J. C. Baker[7] state that by centrifuging potato starch paste with a trace of sodium chloride, they have resolved it into α-amylose or amylo-pectin and β-amylose (the amylose of Maquenne and Roux). The α-amylose separated as a viscous, opalescent layer, on which rested a lighter, clearer, and more limpid liquid containing the β-amylose. The latter solution was filtered, whilst the β-amylose was centrifuged twice with a dilute solution of salt. Sherman and Baker have submitted these preparations to the action of enzymes. They measure what they call the amyloclastic action by Wohlgemuth's iodine method[8] whilst the saccharogenic action is measured by the production of reducing sugar.[9] It was found that the production of maltose from β-amylose by purified pancreatic amylase follows the logarithmic law of unimolecular reactions until three-quarters of the total (apparent) maltose has been formed, when the reaction slackens. Purified "takadiastase" was found to possess, particularly in the early stages, a strong amyloclastic (in the author's sense) activity towards β-amylose, whilst purified malt amylase was characterised by its saccharogenic effect in the later stages of the reaction. With α-amylose (amylopectin) all three amylases showed more effect in the earlier than in the later stages probably owing to the formation of resistant dextrins. Malt amylase was found to produce more maltose than the other enzymes (60–80 % with α-amylose, and 85–95 % with β-amylose) before the solution ceased to give the iodine reaction. Starch pastes made at low temperatures, starch liquefied under pressure, and Lintner's soluble starch were found to resemble the α- rather than the β-substrate in their behaviour towards amylases. The authors conclude that Lintner's soluble starch is well adapted for testing the activities of different amylases.

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[5] *J. Amer. Chem. Soc.*, 1916, **38**, 1877; *J.*, 1916, 1075.

[6] Compare *Ann. Reports*, 1916, **1**, 245.

[7] *J. Amer. Chem. Soc.*, 1916, **38**, 1885; *J.*, 1916, 1076.

[8] *Biochem. Zeitsch.*, 1908, **9**, 10.

[9] *cp.* Sherman and Schlesinger, *J. Amer. Chem. Soc.*, 1913, **35**, 1784.

H. C. Sherman and J. A. Walker[10] have studied the hydrolysis of soluble starch by highly purified malt amylase[11] in neutral and acid solutions and in solutions containing monopotassium phosphate. The amylase used had a power of 1060 on the author's scale[12] or of 1600 on Lintner's scale. Increase in concentration of the enzyme in neutral solutions not only produced more rapid hydrolysis but also increased the final yield of maltose. Addition of optima quantities of hydrochloric acid (0·0002 M), phosphoric acid (0·0005 M) or monopotassium phosphate (0·06 M) accelerated hydrolysis and increased the final yield of maltose, the effects being more marked with the smaller than with the larger enzyme concentration. The optimum H-ion concentration as produced by the three electrolytes was found to be p_H 1 1 (Sorensen). It is noteworthy that twice as much of a given electrolyte is required to produce this optimum reaction in 2 % starch solutions as in 1 % solutions, probably owing to the fixation of the H'-ions by the starch or by the alkali added in the course of its purification. As a result of a very large number of conversions the authors conclude that until about 50 % of the calculated quantity of (apparent) maltose has been produced, the hydrolysis proceeds in accordance with the logarithmic law of unimolecular reactions. Approximately linear relations were observed only during the very early stages of hydrolysis. The reaction constant k of the well known equation of the logarithmic law:

$$1/t \log a/(a-x) = k$$

remains nearly constant under favourable conditions of acidity until about half the theoretical percentage of (apparent) maltose has been produced, after which it falls more or less rapidly, the rate of fall depending to some extent on the acidity of the solution and the concentration of the enzyme

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[10] *J. Amer. Chem. Soc.*, 1917, **39**, 1476; *J.*, 1917, 974.

[11] See *J.*, 1913, 986; 1915, 371.

[12] See *J.*, 1910, 1173.

L. Adler,[13] working under different conditions from those of Sherman and Walker, found that the optimum concentration of H-ions for the action of malt amylase is between p_H 4·0 and 5·2. As the concentration passes these limits in either direction the activity of the enzyme decreases rapidly. The effect of neutral salts he found to be small compared with that of the H-ion concentration.

The work of Sherman and Walker (*loc. cit.*) having established the fact that sodium and potassium chlorides, nitrates, sulphates, and phosphates increase the activity of "highly purified" malt amylase, their influence showing increases from the lowest concentration up to the optimum, A. W. Thomas[14] studied the influence of sodium and potassium bromides. He found that these salts in concentrations below 0·2 grm.-mol. per litre reduced the activity of the enzyme, whilst above this concentration to the optimum they behaved like the other salts.

Working with a preparation of Merck's "diastase" M. A. Rakuzin and C. D. Flier[15] found it to be soluble in water to the extent of 84 %. The solution was optically inactive and gave the biuret, xanthoprotein, Molisch's, and Ostromyslenski's reactions.[16] They found that about 7 % of the "diastase" was adsorbed by moist alumina. The adsorbed portion did not give Ostromyslenski's reaction. None of the enzyme was adsorbed by electro-negative kaolin. So far as can be judged from the abstract of this paper (*loc. cit.*), the authors do not bring forward conclusive evidence in support of their suggestion that by adsorption with alumina the particular enzyme preparation with which they dealt is separated into portions forming dextrin and maltose respectively.

T. Chrzaszcz and A. Joscht[17] have carried out a series of experiments from which they conclude that there is no definite relation between the liquefying and saccharifying powers of malt amylase, and therefore that these two functions are to be ascribed to separate enzymes.[18] The dextrin-forming power may be a resultant of the two first-named functions under conditions not yet determined.

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[13] *Biochem. Zeits.*, 1916, **77**, 146; *J.*, 1917, 230.

[14] *Ibid.*, 1917, **39**, 1501; *J.*, 1917, 974.

[15] *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 321; *J.*, 1917, 300.

[16] See *J.*, 1916, 433.

[17] *Biochem. Zeits.*, 1917, **80**, 211; *J.*, 1917, 901.

[18] See *J.*, 1912, 1089.

In the recent work of J. L. Baker and H. F. E. Hulton on the composition of horse chestnuts and acorns, referred to on page 412, it may be observed that those authors found an amyloclastic enzyme of strong saccharifying but weak liquefying power in horse chestnuts. Acorns on the other hand showed only weak amyloclastic activity. Many years ago Baranetzky failed to find "diastase" in germinated or ungerminated acorns, and he believed his negative result to be due to the presence of tannin.

Data are being accumulated in regard to the formation of enzymes, produced on the one hand during the germination of seeds and on the other hand by the growth of bacteria on various media. In these circumstances some of the enzymes are found in the substrate, the endosperm in the case of germinating seeds, and the nutritive media in the case of bacterial growths, whilst others are found in the embryo of the seeds or in the bacteria themselves. The former group are the so-called endo-enzymes, typical of which are sucrase and amylase, whilst the latter group include the ekto-enzymes, typical of which are maltase and zymase.

A. Boidin and J. Effront[19] have protected a method for the manufacture of enzymes and toxins by aerobic bacteria which are cultivated on media rich in assimilable nitrogenous substances but poor in carbohydrates and fats, *e.g.*, soya bean cake from which has been removed part of the fats and carbohydrates. A very powerful liquefying amylase may be obtained in this way from *B. tyrothrix* or *B. subtilis*.[20] The second patent specification cited mentions *B. mesentericus* or *B. subtilis*.

In a recent paper J. Effront[21] states that by cultivating certain species of *B. mesentericus* on spent grains and feeding cake freed from starch, he has obtained an amylase, which he designates as "acrodextrinase." It liquefies starch paste rapidly, its optimum temperature being 40° C., at which a maximum of 40 % of (apparent) maltose is produced. Its optimum activity is in a medium neutral to methyl orange, but it retains its activity in presence of 1 grm. of sodium carbonate per litre. On the other hand 0·1 grm. of hydrogen chloride per litre completely arrests its activity. The author claims that it is possible to obtain from 1 kilo. of grains a quantity of the liquefying enzyme equivalent to that in 20 kilos. of good malt. The enzyme is recommended for use in the textile industries and for the production of dextrin syrups from the residues of starch factories.

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[19] Eng. Pat., 16,198/1914; *J.*, 1915, 444; 1917, 732.

[20] Eng. Pat. 23,738/1913.

[21] *Comptes rend.*, 1917, **164**, 415; *J.*, 1917, 468.

C. M. Hutchinson and C. S. Ram Ayyar[22] describe an enzymic substance *bakhar*, prepared from rice, powdered roots, and other parts of certain plants by Indian natives, and used in the production of Hindu rice beer (*pachwai*) and of the rice spirit distilled from it. It contains many mould fungi which saccharify starch, the most active being *Aspergillus oryzæ*, besides yeasts capable of producing alcohol. The saccharifying power of *bakhar* is said to be much less than that of Japanese *koji*, which is made from a practically pure culture of *Aspergillus oryzæ*.

A comparison of the yields of furfural formed by distilling barleys and the malts obtained therefrom led J. L. Baker and H. F. E. Hulton[23] to the conclusion that there is a small but distinct production of "furfuroids"[24] from "non-furfuroid" matters during the malting process. Barley embryos, when grown in the dark on sand moistened with sucrose solution, increased in "furfuroid" content. Attached to their own endosperm the embryos increased in "furfuroid" content corresponding with the loss of the same material sustained by the endosperm. Thus there is evidence of the existence of an enzyme capable of hydrolysing "furfuroids." It may be pointed out that J. Gruss[25] showed that the cell wall of the barley endosperm is partially hydrolysed during germination. This cell wall, he adds, in all probability consists of arabanoxylan, since E. Schulze found that the cell walls in the case of rye and wheat consist of that polysaccharide. L. A. Hawkins[26] shows that a filtered aqueous extract of the mould fungus *Glomerella cingulata* contains an enzyme capable of converting xylan into xylose.

Enzymes of Yeast.—According to T. Bokorny[27] sucrase of yeast is not injured when left in contact with absolute alcohol for several days, and he finds that it shows little sensitiveness towards acids. A 1 % solution of caustic soda destroys the enzyme within 24 hours, but 5 % formaldehyde solution does not. Maltase is very sensitive towards alcohol, being injured even by 10 aqueous solutions, whilst a 1 % caustic soda solution destroys the enzyme in a few hours; 1 % hydrochloric, acetic, or lactic acid weakens it in 24 hours; and 0·1 formaldehyde also weakens it. W. A. Davis[28] has shown that maltase is very widely distributed in plants, but he points out that the failure to recognise it is due to the fact that it is an endocellular enzyme, and that it is extremely sensitive towards reagents. Bokorny (*loc. cit.*) states that 50 alcohol destroys zymase within 24 hours. Further, that this enzyme is destroyed by concentrated solutions, but that its action is stimulated by dilute solutions of neutral salts. 1 sulphuric acid destroys it in 24 hours, as does also 5 lactic, acetic, or butyric acid. Its activity is destroyed by 0·05 ammonia in 18 hours, and by 1 formaldehyde in less than 24 hours. Bokorny also makes similar observations on emulsin, rennet, and myrosin, all of which may occur in yeast.

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[22] *Mem. Dept. Agric., India, Bacteriological Series*, 1915, **1**, 137; *J.*, 1916, 751.

[23] *J. Chem. Soc. Trans.*, 1917, **111**, 121; *J.*, 1917, 398.

[24] The use of the term "furfuroid" instead of pentosan appears to the writer undesirable as it might be taken to denote "resembling furfural."

[25] *Wochensch. Brau.*, 1895, **12**, 1257; *J.*, 1896, 464.

[26] *Amer. J. Bot.*, 1915, **2**, 375; *J.*, 1917, 663.

[27] *Allg. Brau.- u. Hopfen-Zeit.*, 1916, **56**, 395, 433, 465; *J.*, 1916, 900.

E. G. Griffin and J. M. Nelson,[29] referring to Beard and Cramer's observation[30] that the activity of sucrase is diminished by the presence of glass beads in the reaction liquid, state that this is due to a lowering of the H-ion concentration by the alkali extracted from the glass. In the same way they explain Eriksson's observations[31] on the weakening of the activity of sucrase by the presence of charcoal, alumina, serum or egg albumin. In a later paper Nelson and Griffin[32] show that when animal charcoal or alumina is added to a solution of sucrase containing buffer salts to maintain the concentration of H-ions, the enzyme is adsorbed but retains its activity. The enzyme re-enters solution when a colloid, *e.g.*, saponin or egg albumin, is added.

Continuing their work on the composition and formation of enzymes, H. Euler and E. Lowenhamm, fermented solutions of sodium pyruvate, to which monosodium phosphate (a buffer salt) had been added to prevent any great change in the concentration of H-ions, with fresh bottom yeast and the same dried to less than 10 of moisture. The fermentative power of the dried yeast was 10–30 lower than that of the fresh yeast. Toluene was without effect on the dried yeast, but it increased the fermentative power of the fresh yeast three to fourfold. It will be remembered that Euler and Johansson, and Euler and Cramer, succeeded in increasing the sucrase content of yeast by cultivating it in certain media.[34] By cultivating yeast in nutrient solutions of sodium pyruvate they succeeded in increasing the carboxylase activity by about 20% only.

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[28] *Biochem. J.*, 1916, **10**, 31.
[29] *J. Amer. Chem. Soc.*, 1916, **38**, 722; *J.*, 1916, 702.
[30] *Proc. Royal Soc.*, 1915, **88**, *B*, 575; *J.*, 1915, [illegible]
[31] *Z. physiol. Chem.*, 1911, **72**, 313; *J.*, 1911, 914.
[32] *J. Amer. Chem. Soc.*, 1916, **38**, 1109; *J.*, 1916, 702.
[33] *Z. physiol. Chem.*, 1916, **97**, 279; *J.*, 1916, 1230.

In a paper by E. Abderhalden and A. Fodor,[35] an experimental study is described on the action of yeast maceration juice[36] on different polypeptides at different concentrations of H-ions. The results support the view that enzymes act as colloidal catalysts in a similar manner to the inorganic catalysts investigated by Bredig. They are not in harmony with the view that an enzyme is active towards a definite grouping of atoms.

C. Neuberg and E. Färber[37] find that 5% sugar solution can be fermented completely by yeast maceration juice in presence of 0·1–0·2 grm.-mol. of sodium or potassium carbonate, potassium metaborate, or tripotassium phosphate, or 0·02 grm.-mol. of sodium or potassium sulphite per litre when these substances are added before fermentation has commenced. When the addition is made after fermentation has started, twice the quantity of the substances does not prevent complete fermentation.

According to T. Bokorny[38] yeast cells may be killed without destroying the activity of zymase by treatment with 0·1–0·5% solutions of sulphuric acid, ammonium and sodium flourides, formaldehyde, ferrous sulphate, ammonium oxalate, potassium chlorate, chloroform, ether, etc. The washed and dried preparations are similar to so-called acetone yeast.[39]

A. Harden[40] shows that zymin (acetone yeast) and dried yeast rendered inactive by washing out the co-enzyme regain their activity by the addition of potassium pyruvate and a phosphate. Carboxylase has been shown to be unaffected by washing, and since acetaldehyde is the first product of the action of this enzyme on pyruvate it was thought that acetaldehyde might also restore the activity of the yeast preparations. This was found to be the case in presence of potassium or ammonium phosphate (not with the sodium salt). Hence it would appear that K- and NH_4-ions possess a specific function not shared by the Na-ion, which is in accord with the fact that sodium phosphate cannot replace the potassium salt in a culture medium for yeast. The experiments support the view that acetaldehyde is an intermediate product in alcoholic fermentation, and that it may be the co-enzyme of yeast juice.

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[34] See *J.*, 1912, 245; 1914, 97.

[35] *Fermentforschung*, 1916, **1**, 533; *J.*, 1917, 663.

[36] Lebedeff, *see Annual Reports*, **1**, 247.

[37] *Biochem. Zeits.*, 1916, **78**, 238; *J.*, 1917, 515.

[38] *Allg. Brau-u. Hopf.-Zeit.*, 1916, **56**, 1547; *J.*, 1917, 300.

[39] A. E. Buchner and R. Rapp, *Ber.*, 1902, **35**, 2376.

[40] *Biochem. J.*, 1917, **11**, 64; *J.*, 1917, 731.

Hop Resins and Oils F. W. Wolff[41] distils hops at a temperature below 100° C. in a current of steam containing alcohol (produced by passing steam through 8[illegible] alcohol), by which means the oils are volatilised and carried over. They are next subjected at a low temperature to vapours produced by passing steam through 67% alcohol, which condense on the hops and extract the soft resins. Finally, the hops are submerged in warm water (with or without a small proportion of alcohol), and then acted on by the vapours of low alcoholic content to dissolve the hard resins. An apparatus for carrying out this process is described.

Caramel[42] About fifty years ago Gelis obtained three substances: caramelan, $C_{12}H_{18}O_9$, caramelen, $C_{36}H_{50}O_{25}$, and caramelin, $C_{24}H_{26}O_{13}$, by heating sucrose at 180–190° C. When the heating was stopped at a stage when the loss in weight was 12%, the product consisted chiefly of caramelan; with a loss of 15% the product was mainly caramelen, whilst with a 22% loss it consisted almost entirely of caramelin. M. Cunningham and C. Dorée[43] have studied caramelan. By heating sucrose as above mentioned they obtained besides caramelan, furfural, pungent acid vapours, and carbon dioxide. Caramelan is a brown gritty powder, very hygroscopic, and melts at 136° C. It is readily soluble in water, and fairly so in 81% alcohol; it reduces silver nitrate and Fehling's solution. A concentrated aqueous solution acidified with hydrochloric acid gives on addition of resorcinol a red precipitate, soluble in alcohol and alkalis. Phloroglucinol gives a similar precipitate, but of a deeper colour. It is probable that the above-given formula should be doubled. Concentrated non-oxidising acids convert caramelan into caramelin. Weaker acids produce dextrose, methylfurfural and humic acid.

Composition of Beers.—A very comprehensive Bulletin has been published by the U.S. Department of Agriculture, Bureau of Chemistry,[44] giving proximate analyses of a great number of different types of beers brewed in the United States. The work was carried out by L. M.

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[41] Eng. Pat. 107,155, 1916; *J.*, 1917, 936.

[42] The writer would point out that the commercial colouring matter known as caramel is obtained by heating sugars in presence of certain other substances, consequently what applies to sugar heated *per se* may not, and probably does not apply to the commercial product.

[43] *Chem. Soc. Trans.*, 1917, 111, 589; *J.*, 1917, 973.

[44] *Bull.* No. 493; see *J.*, 1917, 900.

Tolman and J. G. Riley. Access was secured to several breweries making beers from various raw materials. The authors find that there is a very sharp line of demarcation between the all-malt beers and those made from mixtures of malt, maize, rice, and corn products (? starch sugars). The results show that the percentage of proteins (N × 6·25) is more sharply reduced by the use of malt substitutes than is the ash or phosphoric acid, although where corn (maize) or "cerelin" was used there is a marked reduction in the percentage of phosphoric acid. The authors point out that J. Race,[45] working with English beers, found a reduction of proteins by the use of malt substitutes, as they themselves found. However, the all-malt beers brewed in the United States contain more proteins than those brewed in Europe.

J. S. Sharpe[46] carried out an investigation with some typical British beers to ascertain the quantities of the different classes of nitrogenous compounds present. Unfortunately he does not state the original gravity of the beers he examined. A summary of his results is given on the following page.

He also extracted 0·01 % of an alkaloidal oily substance, which gave many of the reactions of coniine, from stout and smaller quantities from the other beers. This, together with a minute quantity of another oil (perhaps betaine), is said to account for the small quantity of nitrogen shown as undetermined in the table.

ANALYSIS.

Waters.—Apart from freedom from contamination which is of paramount importance in all waters required either directly or indirectly for potable purposes, the greatest attention is now being paid to the saline constituents as influencing the activities of malt enzymes. R. Emslander[47] points out that every enzyme has an optimum temperature, and an optimum concentration of $H^{\cdot}$- or OH'-ions of the medium in which it acts. The influence of a brewing water may accordingly be favourable or unfavourable towards the activity of a given enzyme, according to the character of the saline matter it contains. The transformations due to enzymes which occur in brewing require, in every case, a slightly acid medium. Carbonates are to be regarded as "buffer salts" or "reaction regulators," since in their presence the small quantities of acids derived from the malt scarcely

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[45] *J.*, 1908, 544.

[46] *Biochem., J.*, 1917, **11**, 101; *J.*, 1917, 1059.

[47] *Z. ges. Brauw.*, 1916, **39**, 137.

	Beer (light)		Beer (strong)		Ales		Porter.	
	Tennent's Lager Beer	Draught Beer.	Bass & Co.'s Pale Ale (A)	Bass & Co.'s Pale Ale (B).	Younger's Edinburgh Pale Ale	Worthington's Indian Pale Ale	Allsopp's Special Stout	Guinness's Extra Stout
Total nitrogen	0·049	0·057	0·084	0·082	0·039	0·063	0·056	0·118
Protein nitrogen	0·006	0·021	0·011	0·018	0·010	0·010	0·012	0·029
Amino-acid nitrogen	0·017	0·014	0·036	0·064	0·018	0·016	0·019	—
Purine nitrogen	0·016	0·019	0·039		0·010	0·033	0·020	—
Undetermined nitrogen	0·010	0·003	0·004	—	0·001	0·004	0·005	—
Total solid matter	4·89	3·47	6·37	6·20	4·89	4·[illegible]2	5·90	—
Carbohydrate (dextrin)	2·45	1·30	3·06	3·09	2·46	2·24	2·[illegible]5	—
Specific gravity	1006·8	1006·1	1009·4	1009·0	1008·3	1007·0	1009·9	1010·0
Bottle contained	250 c.c.	550 c.c.	330 c.c.	265 c.c.	7[illegible]5 c.c.	32[illegible] c.c.	305 c.c.	310 c.c.

affect the concentration of H'-ions. Without these buffers a very small addition of acid would cause a very great increase in the concentration of H'-ions. It therefore follows that waters containing very different quantities of carbonates have nearly the same concentration of H'-ions, so that the point of paramount significance in a brewing water is the quantity of total solids, and especially the carbonates which it contains. Instead of the tedious and difficult gravimetric method of estimating total solids in a water, Emslander advocates one based on the measurement of electrical conductivity, and he describes a method devised by Poroschewski and Divoranczyk.[48] The electrode is a pipette having a globular enlargement (3 inches in diameter) and provided with a stopcock below it. The electrode connections are sealed through the walls of the bulb, and the wires carried upwards in two glass tubes are also sealed to the walls so that they are not wet when the apparatus is immersed in the water bath. The two electrodes consist of sheet platinum. The apparatus is immersed in a large water-bath maintained exactly at 18°C., the measurement of resistance being made by the Wheatstone bridge method. For standardising the apparatus a $N/50$ solution of potassium chloride is recommended. This has a specific conductivity of 0·002399 reciprocal ohm. This number, multiplied by the resistance found in standardising, is the resistance capacity of the apparatus, and in all subsequent determinations with waters the specific conductivity is found by dividing this resistance capacity by the observed resistance. The formula for the calculation of the total solids in a water is:—

$$M = C\,k.10^6,$$

where M is the total solids in parts per million, k is the specific conductivity and C a constant, usually 0·695 at 18°C., but for soft waters of high chlorine content (50 parts per million) it is 0·670, whilst for hard waters of low chlorine content (20 parts per million) it is 0·725. For other details of the method, see *J. Inst. Brewing,* 1916, **22**, 504.

In a paper by S. Judd Lewis, Messrs. Murphy and Lonsdale insert some paragraphs[49] recommending the spectrographic analysis of brewing waters. They state that they have obtained unmistakable evidence both in the mashing process and in the fermentation itself that certain elements, which have not been previously suspected, exert a very definite influence. Non-metallic and even rare constituents which have been discharged into the atmosphere from foundries, smelting works and such-like establishments, are mentioned. It is profoundly to be desired that this evidence may be published at no distant date. Bare statements of the kind cannot be accepted.

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[48] *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1489.

[49] *J.*, 1916, 662.

Moisture.—The fact that when calcium carbide is moistened with water a definite volume of acetylene is evolved was first suggested by P. V. Dupré as a basis for the estimation of moisture in ammonium oxalate, and later in cordite.[50] The same principle has since been applied for the estimation of moisture in numerous other substances. W. Windisch and M. Glaubitz[51] find, for example, that the carbide method is a convenient one for the estimation of moisture in barley, hops, malt combs, and yeast. The apparatus devised by Campbell[52] is employed The results are found to be slightly higher than those obtained by drying at 105 C The method, it is stated, can also be used for the estimation of moisture in sugar solutions if the latter are previously absorbed by bibulous paper P. Petit[53] also proposes to make use of this method for the estimation of moisture in barley, malt, and the like. He describes a simple apparatus for carrying out the determinations, which can be constructed readily in the laboratory. The results are within 0·5 of the truth. They are calculated from the volume of mineral oil displaced by the acetylene generated, or from the pressure of the acetylene. Naturally the experiments must be conducted at a constant temperature (110° F. is adopted by Petit), and every operator must standardise his apparatus by a series of tests with materials of known moisture content.

Alcohol.—P. N. Evans[54] has determined what he denotes the boiling and condensing points of mixtures of alcohol and water. A table is given representing the results obtained with 43 different mixtures smoothed out by curves. In each experiment 500 c c. of the mixture was distilled from a Würtz flask of 1 litre capacity at such a rate that one drop passed over per second When 15 c.c. had passed over distillation was stopped and the composition of the distillate was taken as the vapour phase. The average of the composition of the liquid before distillation and of the liquid remaining in the flask after distillation was taken as the liquid phase. The temperature of the vapour in the neck of the distilling flask just below the level of the side tube, when one-half of the 15 c c. had passed over was taken as the boiling point of the liquid. By means of the table the composition of any mixture of alcohol and water may be approximately deduced from its boiling point. The table includes liquids containing from 91 % by weight of alcohol to nil. It will be noted that the author only claims approximate accuracy, whilst it should be remembered that highly accurate results may be obtained much more expeditiously by the specific gravity method.

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[50] *Analyst*, 1905, **30**, 266 1906, **31**, 213, *J*, 1905, 940, 1906, 780

[51] *Wochensch Brau*, 1915, **32**, 389, *J*, 1916, 182.

[52] *J.*, 1913, 67.

[53] *Brasserie et Malterie*, 1916, **6**, 97

[54] *J. Ind. Eng. Chem*, 1916, **8**, 260, *J*, 1916, 483.

A. W. Dox and A. R. Lamb[55] suggest for the accurate determination of alcohol, aspirating air (at the rate of 25 litres an hour for 8–10 hours) through an alcoholic liquid saturated with ammonium sulphate, absorbing the alcohol in concentrated sulphuric acid, and finally oxidising it with bichromate. The resulting acetic acid is estimated in the distillate by titration with standard baryta solution. Acetone is but slightly oxidised under these conditions, but esters must be estimated separately.

W. F. Carthaus[56] draws attention to the error involved in the estimation of alcohol pyknometrically by the distillation method owing to the passing over of volatile constituents from the hops. This is confirmed by G. D. Thevenot[57], who suggests as a remedy making the fermented liquid alkaline before distillation On the other hand A. Fonyo[5 failed to detect any acidity in the distillate of a hopped liquid. He found that the error due to hops was not affected by the addition o calcium carbonate before distillation.

A. Fonyo[59] describes a number of determinations in hopped and unhopped worts to which up to 0·5 % of alcohol had been added The worts were distilled and the specific gravities taken and also the readings of the Zeiss-Pulfrich refractometer.[60] The pyknometric results showed no alcohol in the unhopped wort, but the hopped wor containing no alcohol showed 0·04 %, whilst the results for the hopped worts containing alcohol were all high to the same extent, which i attributed to traces of volatile hop constituents (*vide supra*). Th refractometer results were accurate up to the limit of sensitiveness 0·08 %. It is pointed out that an error of 1° C. in the temperature produces an error of about 0·2 % in the apparent alcohol content. Bacon' method[61] was found satisfactory for worts containing small quantitie of alcohol.

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[55] *J. Amer. Chem. Soc.*, 1916, **38**, 2561; *J.*, 1917, 42.

[56] Commun. Master Brewers' Assoc., *J. Inst. Brewing*, 1917, **23**, 257.

[57] *Ibid.*, 257.

[58] *Ibid.*, 258

[59] *Amer. Brewers' J.*, 1917, **41**, 142; *J.*, 1917, 515

[60] *cp.* Ackermann and Steinmann, *J.*, 1905, 563; Barnard, 1907, 707.

[61] *J.*, 1912, 42.

Detection and estimation of small quantities of methyl alcoho in ethyl alcohol.—E. Elvove[62], employing Denigès' method,[63] finds that the delicacy is increased by reducing the proportion of ethyl alcohol to 0·5 by volume, as little as 0·1 mgrm. of methyl alcohol in 5 c.c. then giving the coloration with Schiff's reagent after standing for 10 minutes.

Acidity.—A. Reichard[64] recommends the employment of two indicators litmus and phenolphthalein in titrating barley and malt extracts, worts, and beers. He points out that the increase in acidity ssociated with the first stages of germination in the malting process is ue mainly to the formation of very feebly acid substances which react owards phenolphthalein but not towards litmus The acidity eveloped during the fermentation of wort, on the other hand, is due ainly to substances which react towards litmus He is of opinion hat the stability of a beer depends not so much on the total acidity etermined with phenolphthalein as upon a high litmus acidity in elation to total acidity.

Starch—Ewers' acid hydrolysis method of estimating starch was eferred to in the previous Report[65]. C. Baumann and J. Grossfeld[66] ake use of the fact that starch is completely precipitated by lead annate when the latter is formed in the starch solution, to correct for he optical effects of other substances on the accuracy of this method. he starch having been dissolved, basic lead acetate and tannin are dded. The filtrate is then submitted to Ewers' conditions of hydroysis whilst a further portion of the sample is submitted to the same reatment without addition of lead tannate. The difference between he optical rotations of the two liquids is then calculated to starch. von Fellenberg[67] proposes to estimate starch by a direct gravimetric ethod depending on heating the starch with 50 % calcium chloride olution, and adding $N/50$ iodine to the filtrate (a large excess of iodine ust be avoided). The precipitate is collected in a Gooch crucible nd washed with alcohol first of 85 % strength till colourless, then with lcohol of 90 % strength, and finally with hot and cold alcohol succesively. The crude starch is weighed dry and corrected for ash.

Pentosans.—J. L. Baker and H. F. E. Hulton[68] have further revised

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[62] *J. Ind Eng Chem*, 1917, **9**, 295, *J*, 1917, 168.

[63] *J*, 1910, 585

[64] *Zeits. ges Brauw*, 1916, **39**, 313, 322, 329, 337, 345, 353; *J*, 1917, 399

[65] Vol. 1, p 258.

[66] *Z. Unters. Nahr. Genussm*, 1917, **33**, 97, *J*, 1917, 662

[67] *Mitt Lebensmittelunters Hyg.*, 1916, **7**, 369; *J*, 1917, 935.

[68] *Analyst*, 1916, **41**, 294, *J.*, 1916, 1127.

Flohil's method of estimating pentoses and pentosans[69] which was modified by Eynon and Lane.[70] The method depends on distillation with hydrochloric acid under the conditions laid down by Tollens, neutralising an aliquot portion of the distillate, heating with an excess of Fehling's solution in a boiling water bath. Eynon and Lane heated the mixture over a flame. When the heating is conducted in a water bath the correction for sodium chloride is much less.

Amino-nitrogen.—A modification of Van Slyke's method for the gasometric estimation of amino-nitrogen in worts, &c., is described by R. Emslander.[71]

Interference refractometry.—The principle of instruments depending on interference of light is described by R. S. Willows.[72] Great delicacy is attainable by such instruments, which are based on Lord Rayleigh's discoveries in 1896. These instruments are now manufactured by a London firm. The use of such an instrument in the brewery laboratory is discussed by L. Adler and H. Leurs.[73]

AGRICULTURAL EXPERIMENTS.

Barleys.—An interesting account is given[74] of field experiments with different varieties of oats and barleys, carried out at Cockle Park; the Harper Adams College; Garforth; the Midland Agricultural College; also in East Suffolk; and Essex. As regards the barleys, the results appear to point to the superiority of Goldthorpe types in the northern experiments, and to some extent this is true in the case of the Midland experiments where Chevaliers, more especially the Archer variety, although producing the heaviest yield, gave a grain which in dull seasons was not of the best quality; in East Anglia Chevalier types seem still to hold their own. Accurate deductions are, however, difficult to make, as the points to be considered are not only yields, but also malting qualities.

Since the year 1906 numerous papers have been published by H. Schjerning, dealing with the metabolism of the proteins of barley during the malting and brewing processes.[75] In a posthumous paper published in conjunction with J. Hempel[76] an account is given of an investigation, the object of which was to ascertain whether the malting quality of a barley is hereditary, and if so how far it may be affected by the nature of the soil. The problem is left practically unsolved, as the data at present accumulated are insufficient One of the varieties studied, however, namely, Golden barley, appeared when malted to be characterised by deficiency in the power of producing enzymes. It would seem that size of corn is a racial characteristic.

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[69] *Chem. Weekblad*, 1910, **7**, 1057

[70] See *J.*, 1912, 259

[71] *Zeits. ges. Brauw.*, 1916, **39**, 265; *J.*, 1917, 399.

[72] *J. Inst. Brewing*, 1917, **23**, 459

[73] *Zeits. ges. Brauw.*, 1916, 39, 17, 25, 33, 41; *J.*, *Inst. Brewing*, 1916, **22**, 504

[74] *J. Board of Agric.*, 1917, **23**, 1056.

[75] *See* Ann. Reports, **1**, 246, 252

[76] *Comptes rend. Trav. Lab. Carlsberg*, 1917, **11**, 333; *J.*, 1917, 973.

Hops.- In a comprehensive paper on the value of hop breeding experiments, E. S. Salmon[77] brings forward his own evidence as also that of other observers, whom he quotes, *e g*, J Topham Richardson, S. Sneed, W. W. Stockberger, G Arnold, and J Schmidt, to show that the aroma of hops is a racial characteristic which does not change as some have asserted, when the hops are transplanted, as cuttings to other countries. He has been engaged for many years in attempts to obtain hybrid hops which have definite characteristics. Here, however, a great difficulty is encountered, for the hop is a dioecious plant Hence Mendelian principles cannot be applied, for the characters of the female plant alone are known, those of the male plant being a lottery Breeding experiments in the case of hops are therefore largely a matter of chance. As an instance of this Salmon quotes an interesting episode A certain hop picker emptied out the crumbs from her dinner basket on to her garden, and by chance a hop seed was among the crumbs. This grew up to be a seedling, the valuable character of which Mr. Fuggle of Brenchley, had the good sense to recognise. Hence arose the Fuggles hop The most recent achievement of Salmon is to have obtained a hop which is resistant to mildew (*Sphaerotheca Humuli*)[78]

F. Ancker[79] quotes field experiments of several farmers on the manuring of hops with special reference to the effect of potash salts. Generally it was found that 75 lb. of potash salt (10 "*Kalidungesalz*") per acre (the quantity of sulphate of ammonia and superphosphate being kept constant) produced not only the best yield but the best quality of hops. When, however, the quantity of potash was raised to 115 lb. per acre, the yield of hops was further increased, but the quality was inferior, probably owing to a greater development of leaves

MALTING.

General.—Although remaining largely an empirical art, additions to our knowledge in the domain of plant physiology are surely if slowly tending to help in giving us an accurate insight into the nature of the changes which occur during the malting of grain. When some 30 years ago the system of pneumatic- or to describe it more correctly mechanical – malting was proposed by Galland, it was anticipated that it would in time replace the time-honoured flooring system, as it tended towards making the maltster independent of external changes in weather conditions and also held out the prospect of enabling him to continue malting throughout the entire year. Yet, despite numerous improvements in the mechanical system, the fact remains that the bulk of the malt used in this country is still made on the floors. Perhaps one of the chief reasons that the new system has failed to replace the old is that its pneumatic features have been abused. Aëration has been adopted at stages of the malting process at which it was not required, nay, at which it was actually harmful. In discussing a paper by J. Sleeman, who has done much to develop so-called pneumatic malting in this country, H. T. Brown[80] pointed out that the really weak point in pneumatic malting, putting all questions of cost on one side, appeared to him to be the difficulty of checking the respiratory processes of the grain towards the finish of germination. The couches could only be cooled by passing through them an abundance of air and this at a time when it was necessary to check respiration and the formation of new tissue by the plantlet. He observed that on the old flooring system the couches were kept down in temperature by a certain amount of radiation from the surface layers, but mainly by the constant and large evaporation of water which was going on from the surface of every grain of malt. It was only occasionally at the time of turning that each grain was bathed for a short time with a full supply of air. As the malt laid in the couch, especially in the later stages, each corn surrounded itself with an atmosphere extremely poor in oxygen and very rich in carbonic acid. This carbonic acid was only replaced with air by the slow processes of gaseous diffusion and the partial asphyxiation of the embryo so brought about, retarded the respiration and consequently the active growth. Such checking of respiration by the limitation of air was, said Brown, very necessary for the production of first-class malts, which were required for the infusion processes of brewing; for it was at this period that the several enzymes which were secreted by the embryo got an opportunity of thoroughly permeating the endosperm, so producing that mellowness in the green malt, and that friability in the finished malt, which was so characteristic of good samples.

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[77] *J. Inst. Brewing*, 1917, **23**, 60.

[78] *J Agric Science*, 1917, **8**, 455

[79] *Wochensch. Brau.*, 1916, **33**, 273.

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[80] *Trans. Inst Brewing*, 1891, 5, 43

The writer of this report is quite convinced of the truth of Brown's statements, and he has insisted for many years on the value of withering in the production of well modified malt, basing his views on experimental data.[81] The promoters of the pneumatic process have endeavoured to remedy the defects in the process by suggesting that the early stages of kilning should be carried out on an ordinary kiln instead of in a drum, the final curing being conducted in a special drum. This, it must be admitted, has constituted an improvement, but the fact still remains that what may be termed the floor withering is not provided for and would still be conducted in a drum under conditions of some aeration. A considerable advance has been made by the Kropff system, which consists in allowing the barley to germinate either on the floors or in a drum and conducting the final stages of germination in a vessel (usually a box) in which the carbon dioxide produced by respiration is allowed to accumulate for periods of 12–21 hours, after each of which periods the piece is aerated. Reports on the process have been published by C. Bleisch,[82] and by F. Schonfeld.[83] L. Adler[84] malted a sample of 1911 barley by the floor, drum, and Kropff systems respectively, and concluded that the Kropff malt was the best in every respect, the floor malt coming next.

L. Pierre[85] suggests that, in the Saladin box-malting system, when mechanical turners cannot be installed, instead of several boxes, a single long box divided below its false bottom into as many compartments as there are days of germination should be adopted. All the compartments communicate with an air-duct in such a way that the supply of air to each can be controlled at will independently of the others. The arrangement really represents a "series" of Saladin boxes without dividing walls between them, the width of each compartment being such that the grain can be transferred from one to the next by a single throw of the shovel. The steeped barley is first loaded on the false bottom of the first compartment until after the eighth it is discharged from the last compartment. This author falls into the error of many others of assuming that the cooling agent in every malting system is air: it is not. Air is the vehicle which takes away the moisture and it is evaporation which lowers the temperature.

Steeping.—L. Pierre (*loc. cit.*, 1917) draws attention to the advantages attending the addition of hydrogen peroxide to the steeping cistern in promoting germination. He believes that other less costly oxidising agents might also be used. In this connection the observation of Czerny[86] that the use of hypochlorite in the steeping cistern improves the germination of barley may be recalled.

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[81] *J. Inst. Brewing*, 1908, **14**, 491; 1912, **18**, 436, 590; *J.*, 1908, 1033; 1912, 740, 789.

[82] *Zeits. ges. Brauw.*, 1911, **34**, 209; 1912, **35**, 217.

[83] *Wochensch. Brau.*, 1913, **30**, 354, 374.

[84] *Zeits. ges. Brauw.*, 1916, **29**, 201, 217, 225; *J.*, 1917, 156.

[85] *Brasserie et Malterie*, 1916, **6**, 321, 353.

Sprinkling with acid phosphate.—F. Lehmann[87] describes an experiment in which a piece of green malt just commencing to chit was divided, one part being sprinkled with plain water and the other wit a solution of acid phosphate twice daily until the final stage of germination was reached. The piece treated with the phosphate had fresher, cleaner odour, than the other; and although both received th same treatment on the kiln, the finished malt from the former was o a better quality, paler in colour, and yielded in the laboratory 1·5 more extract than the malt sprinkled with water only.

Malt kilns.—P. Petit[88] draws attention to certain defects in mal kilns, the multiple floor kiln being in his opinion better than the singl floor kiln. He suggests that better draught might be obtained by th employment of a suitably modified drum or case for the early stage of kilning. Such a case should be capable of receiving green malt 31 35 inches in depth, and heated air should be drawn through this case b means of a fan. In another paper[89] he adduces arguments which lea him to the opinion that the kiln need only consist of a simple casin with a metallic floor, surmounted by a chamber of brick or masonr provided with a short chimney; further, that the floor need only b a short distance above the ground.

L. Pietre[90] states that in France the method of heating kilns b radiators has replaced that of passing the products of combustio through the malt. He considers the older method preferable o economic grounds, provided the kiln be properly constructed.

It should be pointed out that in Great Britain the most commo fault is too rapid drying, and more especially the use of too hig temperatures at the early stages of kilning. Economy in drying mu give place to methods which will produce the material required by t British brewer, which is well known to be very different from th employed abroad.

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[86] *Oesterr. Brau- und Hopfen-Zeit.*, 1900, No. 1; *J. Inst. Brewing*, 190 **6**, 128.

[87] *Wochensch. Brau*, 1917, **33**, 281; *J.*, 1917, 515.

[88] *Brasserie et Malterie*, 1915, **5**, 378, 393.

[89] *Ibid.*, 1916, **6**, 225.

[90] *Ibid.*, 1916, **6**, 321, 353.

Malt combs.[91]—A. Baumann,[92] in a lengthy paper on this subject, arrived at the following general conclusions: Combs from the malt-cleaning machine are in general poorer in nitrogenous substances than those from the kiln, but the latter usually contain less carbohydrate. The nitrogen-content of the different kinds varies within wide limits, according to the quality of the barley used and also the treatment of the malt during germination. Estimations of extract made on malt-combs led to no satisfactory results. They showed small differences according as to whether the extraction was carried out with or without the aid of malt extract. For the valuation of malt-combs the determination of extract appears to be quite unsuitable. Sucrose is a noteworthy constituent of malt-combs. Their very marked swelling capacity is probably due to the presence of gummy substances, the most important of which is a xylan. Malt combs contain not only proteoclastic enzymes, but others which act on carbohydrates. When an extract of malt-combs is fermented, proteins as well as amino-acids are consumed by the yeast. The yeast multiplies to almost double the extent to which it does in a similarly prepared extract of malt.

BREWING.

General.—Those who are acquainted with the developments going on in different parts of the world in brewing technology cannot fail to be struck with the importance which is now being attached to utilising other enzymes besides amylase, this being attempted by adjusting temperatures and the concentration of $H^{\cdot}$-ions in the medium. More particularly this has been applied to bringing into action the proteoclastic enzymes of malt.

Brewing waters.—The paper of W. Windisch and Goldlacker[93] is interesting as a further contribution to our knowledge of the effect of the saline constituents of water on brewing. The effect of alkaline-earth carbonates, *e.g.*, calcium carbonate, is to decrease acidity by converting primary potassium phosphate into a mixture of secondary potassium phosphate and insoluble tertiary calcium phosphate, whilst the effect of gypsum is to increase acidity by transforming secondary into primary phosphates. A series of laboratory experiments were carried out in which waters containing various combinations of salts were boiled without and with potassium lactate (as representing organic acid salts derived from malt). The larger the quantity of organic salts present the more phosphate can be brought into reaction with gypsum. It is shown that in presence of lactate the alkaline-earths form secondary and not tertiary phosphates. It must be remembered that secondary calcium phosphate is insoluble, whilst the magnesium salt is soluble. The authors draw attention to the high percentage of magnesium salts in malts which are traceable to the manuring of the barleys. Bearing in mind the undesirable influence of magnesium salts in reducing the acidity of worts, it is suggested that the percentage of magnesium compounds present in barley ought to be taken into account in valuing the grain. Magnesium salts tend to prevent the precipitation of calcium phosphate in presence of potassium lactate.

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[91] The writer would here draw attention to the practice which is now almost general of describing malt rootlets as malt "culms", the latter word, being derived from the Latin *culmus*, a stalk, is obviously wrong

[92] *Zeits. ges. Brauw.*, 1916, **39**, 363, 372, 379, 387, 396, 404, 413.

[93] *Wochensch. Brau.*, 1916, **33**, 345.

To remove alkaline-earth compounds from brewing waters the authors recommend treatment with lime. Titration with *N*/10 hydrochloric acid and methyl orange gives the quantity of lime required to convert bicarbonates into normal carbonates, whilst titration with saturated lime water, using phenolphthalein as indicator, gives the free carbonic acid. Since the titration only proceeds to the bicarbonate stage, the amount of lime indicated must be doubled to produce normal calcium carbonate.

Many of the new suggestions put forward in regard to low initial mashing temperatures in order to obtain a better effect of the proteoclastic enzymes of malt are difficult to carry out in the ordinary mashing plant of to-day, and this affords a good opportunity for the observation that the time has arrived for revolutionising this plant. The mash tun with false bottom is at best a patched-up arrangement. Originally a simple infusion vessel in which the mash was mixed by means of oars worked by hand, external mashers, internal rakes and drawing-off arrangements have been successively applied to it, and still it is far from satisfactory. There can be no doubt that a properly constructed closed converter allows of much more latitude as regards the fixation of exact mashing temperatures. And, moreover, it can be used in conjunction with a filter press, thereby not only securing greater uniformity in the composition of the wort, but also saving much time and securing better extracts. Attention was called to this matter in the last Report (Vol. 1, p. 255), and the writer's reason for mentioning it again will be obvious from the observations of different authorities cited in this Report.

Brewing in Germany.—That most prolific writer, W. Windisch, has, as usual, produced a number of papers. These deal principally with the brewing methods which have had to be adopted in Germany on account of the war. In one of these papers[94] he recommends a preliminary soaking of the malt at a temperature below that at which enzymic actions can take place, which effects the softening of any hard unmodified portions of the malt. The process, he states, was practised in former times, especially in Bavarian breweries. In cases where the water supply is rich in carbonates it is recommended to separate the grits and flour from the husks and to submit the former only to the pre-mashing process, especially in the brewing of pale ales. The temperature of the preliminary mash is given as 40°–50° F. (cp. however below), and this may be maintained for from 6–12 hours. If the preliminary mash be as high as 70°–90° F. acids are formed which interfere with subsequent saccharification[95]. Following this soaking (the husks having been reunited in the special cases referred to), the mash is held for about half an hour at 132° F. This is denoted by the author "Protein-rest," a somewhat misleading term. What is meant to be conveyed is that the proteoclastic enzymes of the malt then exert their activities. In decoction mashing the author recommends a "protein-rest" before and after boiling. The latter is effected by returning the boiled portion of the mash to the main, unboiled portion at such a temperature that the mixture does not greatly exceed a temperature of 132° F. For diffusion mashing as practised in this country, the carrying out of these suggestions might present some difficulties, but these would be minimised if a converter in conjunction with a filter press were used in the place of an ordinary mash tun with false bottom.

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[94] *Wochensch. Brau.*, 1916, **33**, 105, 121; *J.*, 1916, 1170.

[95] F. Emslander (*ibid.*, 1916, **33**, 169; *J.*, 1917, 56) finds that with a hard water containing calcium and magnesium salts, pre-mashing renders beer more difficult to clarify. This was counteracted by boiling the water for half an hour before use. Probably when soft brewing waters are used, the effects of pre-mashing would be such as have been observed by Windisch (*vide supra*). During mashing the concentration of H ions increases, but pre-mashing, whilst it increases the acidity of a wort, reduces the concentration of H ions. Evidence is brought forward in support of the view that protein turbidity and sensitiveness towards chill of a beer are due to compounds of proteins with alkalis. A U-tube fitted with two electrodes, one in each limb, was filled with beer and a current of 110 volts passed through it. The U-tube was after stopping the current plunged into ice-cold water, when cloudiness was produced in the anodic limb, from which the author concludes that the particles which give rise to haze are negatively charged and therefore alkaline in character.

F. Lehmann[96] endorses Windisch's opinion of pre-mashing and "protein-rest." He states that to obtain satisfactory results with the "protein-rest," the acidity of the mash must be sufficiently high to stimulate the proteoclastic enzyme, but whether the chief rôle is played by lactic acid or acid phosphates is doubtful. Lehmann observes that when a malt extract, prepared in the cold, is slowly heated to 122° F., a separation of flocculent protein matters commences at 86° F.; but that this does not occur if the extract be first treated with a small quantity of phosphoric acid or acid phosphates. In these circumstances the extract is said to remain clear after the "protein-rest," after boiling, and after chilling. The results obtained by pre-mashing and "protein-rest" are according to Lehmann influenced largely by the salts in the brewing water. Carbonates being "buffer" salts act prejudicially. Magnesia in a water forms insoluble secondary phosphates and thus removes from solution a part of the acid phosphates.

It is interesting to compare the papers above referred to with a later one by W. Windisch.[97] In this paper the author reviews practically the whole of his recent research work. He points out how the prolongation of the war far beyond its expected limits has affected the German brewing industry adversely through the scarcity of labour and materials and that these difficulties have been met by the brewing of lighter beers. These war beers proved much more satisfactory than was anticipated in respect of palate fulness and flavour and still more so in respect of "head" retention. The malts from the 1915 barleys often contained 20, 30, or even 40 of imperfectly modified corns, and they furnished grists therefore similar to that recommended for many years by the author, *i.e.*, short grown malt in conjunction with 20 40 of "chit" malt. This latter consists of barley steeped and couched and, as soon as sprouting has commenced, loaded on kiln.

The plan adopted for dealing with the malts of the 1915 barley was to grind them to a fine grist, to soak the latter in water overnight at a temperature not below 68°–77° F.—a lower temperature (*cp.* above) was found to give a bad flavoured beer—and separate into a thick mash and a thin mash. The former was maintained at 122° F. for about half an hour and then raised to the temperature of saccharification, 148°–158° F. After saccharification the thick mash was boiled. The boiled thick mash was then mixed with the thin mash, the temperature being previously so adjusted that the temperature of the mixture was 122° F., at which it was held for about half an hour. The author states that if this process be adopted with waters containing carbonates a nauseous flavour is developed. The best water to use is said to be one containing little or no mineral matter or a gypseous water.

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[96] *Ibid.*, 1916, **33**, 281; *J.*, 1917, 815.

[97] *Ibid.*, 1917, **34**, 1, 9, 17, 25, 33, 41, 49, 57, 65, 73, 81, 93, 101, 113, 121, 129; *J.*, 1917, 1188.

We gather from the author's remarks that the beers which are now produced in Germany are brewed at an original gravity not exceeding 1036, and, as is the experience in Great Britain with such light beers, there is a difficulty in obtaining a sufficient yeast crop for subsequent gyles. The author suggests a plan which is also adopted by some brewers in this country, namely, to brew two beers, one of higher and one of lower original gravity, and to mix them so that the mixture has the desired original gravity The higher gravity wort will then furnish the yeast crop (*cp.* also p. 135) But Windisch avers that a mixed beer of the kind described *drinks fuller* than one brewed direct at the desired original gravity. In the case of pale ales he is of opinion that it is not advisable to attempt to improve palate fulness by producing worts of high dextrin content. He considers, on the other hand, that the most important factor in regard to fulness is the maintenance of a high ratio of alcohol to extract

Dealing with economy of working in the brewery, Windisch dilates at length on the advantages of the mash filter as compared with the mash tun and also on those of grinding the malt to a fine grist 10 15 of meal and the remainder fine grits and he advocates the use of the modern six-roll mills Finally, he deals with certain scientific considerations, notably the effect of different salts in brewing waters. His views on this subject are well known

K. Windisch[98] points out that since the quantity of malt available for brewing in Germany (except in Bavaria) is only about 15 of the quantity used before the war, it has been necessary to reduce the gravity of the worts to 1020 or even to 1012 The special measures which the brewing of these thin beers demands are discussed by the author who takes as his text a pamphlet on the subject issued by the German Brewers' Union. The majority of the recommendations are similar to those advocated by W. Windisch (*loc cit*). For the light beers referred to, hops must be employed in liberal quantities; thus for a beer of original gravity 1012, 3–4 lb. of hops should be used per 7·3 barrels for dark beers, or 1 5 lb. in the case of pale beers.

The problem of the production of light war ales is further dealt with by W. Windisch and different other writers. Windisch states[99] that infusion methods of mashing have been tried with satisfactory results as regards brilliancy and "head" retention of the beers, and that this innovation has proved beneficial to the yeast crop. It appears that a wort of gravity 1022 is fermented with an energetic yeast, so that suspended hop resins and proteins are removed, and it is then diluted with hop decoction to the desired original gravity.

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[98] *Ibid.*, 1917, **34**, 213, 224; *J.*, 1917, 1188.

[99] *Wochensch. Brau.*, 1917, **34**, 319.

P. Mumme[100] endorses generally Windisch's views. He ferments a wort of gravity 1030, and dilutes it subsequently, preferably with hop decoction. The hop decoction is distributed in a number of small maturing casks and brought with gyle wort to a gravity of 1012. After fermentation these casks are bunged down and the filtered contents used for diluting the stronger beer. We gather that for some of these beers a top fermentation system is employed. Later Windisch[101] recommends diluting a stronger beer with water instead of hop decoction, the use of the latter being due to the erroneous view that the addition of water would be illegal. The beer is subsequently carbonated. The stability of the beers is said to be improved by diluting with water, whilst the undesirable hop bitter flavour is not encountered. The writer would point out that whenever water is used for breaking down beer, it should previously be boiled to remove the air.

Cooling and flocculating worts. L. Heinz[102] discusses the factors which determine the separation of protein matters from worts. He lays great stress on the effect of tannins, and refers to the work of H. T. Brown, who showed the beneficial effects of agitation at certain temperatures on the "break" of wort. In the case of the worts of an original gravity of 1010–1018, the most important factor in ensuring a good "break" during the cooling of the wort, he found to be the presence of the protein substances coagulated by the boiling process. In the absence of these coagulated proteins, agitation alone had little effect on the "break." He points out that in the Wooldridge process described by Ling and Wooldridge (Ann. Reports, **1**, 254), the wort is boiled and cooled under constantly reduced pressure, and this necessarily maintains proteins in suspension. Heinz[103] proposes a new method of cooling worts in a closed cooler. In this the flocculating influence of the coagulated proteins is utilised fully. The hot wort from the hop back is run into a rectangular cooler to a depth of 3 to 5 ft. Suspended within this vessel are a number of cooling tubes, resembling a vertical refrigerator, through which water is passed. The units are arranged 18 in. apart to allow a workman to pass for cleaning. An agitator is also fixed within the vessel, so that the wort is kept in motion during the cooling. It should be noted that this method depends entirely on conduction for cooling—a much slower process than one depending on evaporation as in the Wooldridge system.

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[100] *Ibid.*, 1917, **34**, 320.

[101] *Ibid.*, 1917, **34**, 335.

[102] *Ibid.*, 1917, **34**, 221, 230.

[103] *J. Inst. Brewing*, 1913, **19**, 81.

Malt substitutes.—The present conditions have affected the supply of malt substitutes which are well known to be so necessary for the production of certain kinds of British beers, more especially those of the lighter type. Maize has been scarce and it has been found necessary to restrict its use in brewing, but perhaps the most serious restriction in malt substitutes has been that of brewing sugars, which for the majority of British beers are indispensable. The Sugar (Brewers Restriction) Order, 1917,[104] prohibits the use by brewers of any saccharine substance other than solid glucose or invert sugar or any other product obtained from low-grade cane sugar polarising not over 89, from which 40 % of its weight in the form of "crystal sugar or grocery syrup or grocery honey sugar" has been extracted. The order further includes any caramelised products of solid glucose or invert sugar from the low grade cane sugar hereinbefore described, and mixtures of solid glucose, and the invert sugar and caramelised products. The total quantity of these saccharine substances which brewers are permitted to use is not more than 40 % of the quantity used by them in the year 1915. It is remarkable that the partially converted syrup known as dextrin-maltose which many brewers have found so useful is not mentioned in the order.

In Germany and Austria where the use of brewing sugar was, prior to the war, in most parts of these countries prohibited, it has been found expedient to employ them. Thus we are told by F. Schonfeld[105] that by a statute of 1909 the use of cane sugar as an adjunct in brewing is permitted provided that top-fermentation yeast is used in the primary fermentation. The same author[106] refers also to the use of starch sugars in brewing. V. Kondelka[107] points out that in Austria it is permissible to replace 30 % of the malt used for brewing by sugar, and that potato starch may also be used.

Discussing the suitability of various materials as malt adjuncts,

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[104] *J.*, 1917, 1202.

[105] *Wochensch. Brau.*, 1916, **33**, 9; *J.*, 1916, 858.

[106] *Ibid.* 1916, **33**, 97.

[107] *Allgem. Zeitsch. Bierbrau und Malzfabr.*, 1916, **44**, 71; *J.*, 1917, 399.

P. Petit[108] states that with the French malts now available the use of such substitutes is desirable to avoid haze. About twelve years ago several breweries used manioc which gave excellent yields of extract and was cheap. He refers to the presence of a cyanogenetic glucoside. The traces of cyanide produced from this were, however, entirely eliminated by the brewing process. The writer from an extensive experience in the use of manioc in brewing can confirm Petit's statements. He found, however, that a peculiar bitter flavour came through in the beers when low grade ground manioc was used. This can be prevented to a large extent, probably entirely, by decreasing the quantity of fibre in the manioc which can be done by mechanical means in the dry Petit refers to Windisch's "chit" malt (*see* page 430), but he arrives at the conclusion that raw barley, used to the extent of 10 to 12%, has greater advantages as all expenses of malting are saved.

The rhizome of couch grass, *Triticum repens*, contains a reserve carbohydrate which yields lævulose when treated with acids or diastase. F. Koritschoner[109] deals with the possibility of using this substance in brewing. It yielded extracts ranging from 15 to 22 %, and this low extract combined with the unpleasant odour and flavour rules it out as a brewing material.

Refined adjuncts.—P. Dreesbach[110] puts forward a strong plea for the employment of "refined adjuncts" in the place of raw grain containing protein and oil. The proteins of raw grains, he points out, are of no service as yeast foods,[111] whilst the oils tend to impart an objectionable flavour to the beer. He advocates strongly the advantages attending the use of brewing sugars, especially of those containing high percentages of dextrins, since it is difficult to produce, in the mash tun, worts containing a high percentage of unfermentable matters.

Use of bran in brewing.—R. Wahl[112] draws attention to the secretion of amylase in the aleurone layer of seeds, and he proposes to utilise bran such as the offal of pearl barley or the cortex of maize produced in hominy mills as a brewing material. These materials are mixed with water and maintained at such a temperature (121° F. is suggested) that lactic acid bacteria such as *Bacillus Delbrucki* can develop. The tertiary phosphates are converted into secondary and primary phosphates, whilst the proteins are hydrolysed by the proteoclastic enzymes.

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[108] *Brasserie et Malterie*, 1917, **7**, 429; *J.*, 1918, 102A.

[109] *Chem.-Zeit.*, 1917, **41**, 797; *J.*, 1918, 102A.

[110] *J. Amer. Soc. Brew. Technology*, 1916, **6**, 137; *J.*, 1917, 1106.

[111] Cp. Wyatt and Schlichting, *J., Inst. Brewing*, 1909, **15**, 684, see *J.*, 1909, 733.

[112] U.S. Pat., 1,178,039 of 1916; *J.*, 1916, 650.

Gelatinised starch is then added to this mash, and in this way a wort is obtained suitable for the production of beers. Further details of this work are given by Wahl.[113]

Fermentation and yeast out-crop.—This is a matter which is attracting the attention of every brewer now that beers are brewed at such low gravities. In most cases it has been found possible to meet the difficulty to some extent by brewing two beers, one at a higher gravity and a second at a lower gravity than that at which the beer is to be sent out Thus P. K. Le May[114] cites a case of a brewer turning out a beer of 1036 -the lowest gravity Government ale. He might brew one half at 1042 and the other half at 1030, and blend them afterwards. The writer of this report has found that beers of a greater difference of gravity than those cited are preferable. For example, if it is possible to brew one beer at a gravity as high as 1055, then provided good materials are employed a satisfactory yeast crop and good vigorous yeast will be obtained This necessitates, however, brewing the other beer with which the first is mixed at a correspondingly lower gravity. There is no doubt that at the present time the use of yeast foods in the fermenting vessel is desirable.

F. Schonfeld and C Goslich[115] make some suggestions with regard to increasing the yeast crop in light worts. Their remarks apply to worts of a gravity of 1009 1018, and to bottom fermentation yeast. Their chief recommendations are to aërate at suitable temperatures and to stimulate the yeast before pitching by treating it for a few hours in sweet wort of a gravity of 1010 1018, so that it commences to bud.

Sterilisation of beer by filtration—E. Zahm[116] points out that the sterilisation of beer by pasteurisation affects its flavour and character injuriously. It also arrests or destroys the action of the enzymes, so that the dietetic value of the beer is impaired. Ordinary filter pulp does not sterilise beer efficiently, not because the fibres are incapable of holding back micro-organisms, but because of the mobility of the material under fluctuations of pressure. Rigid filtering beds are, therefore, in the author's opinion, absolutely necessary. He describes a process of sterilising beer by filtering it through kieselguhr compressed into blocks in a moist condition and subsequently fired. The arrangements are described with the aid of drawings. The filters comprise a pair of units, each containing 55 filter cylinders, and the beer is pumped through a pressure governor into the inlet chambers of the units passing through the filter cylinders into the outlet chambers and thence to the bottling machine. The apparatus is sterilised with hot water at 180° F. before use, and then it is tested collectively by displacing the water in the inlet chamber with carbon dioxide under a pressure of 6 lb. In the event of a defective tube, bubbles of gas will be seen rising through the water, and the cover must be removed and the tube plugged. A filter with 110 cylinders has a capacity of 50 pint bottles per hour.

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[113] *Amer. Brewers' Review*, 1917, 31, see *Brewers' Journal*, 1917, **53**, 505.

[114] *J. Inst. Brewing*, 1917, 442

[115] *Wochensch. Brau.*, 1917, **34**, 205, *J.*, 1917, 1189.

[116] *Western Brewer*, 1916, **47**, 217; *J*, 1917, 156.

Chill-proof beer.—In 1911 a process of rendering beer chill-proof was protected by L. Wallerstein.[117] It consists in treating the beer before bottling and pasteurising with a proteoclastic enzyme—pepsin and papain are mentioned—whereby the proteins are converted into substances which are not precipitated when the beer is subjected to low temperatures. The process is claimed to replace chilling in the production of so-called 'non-deposit' beers. P. Petit[118] has tested this process with different classes of beer in several breweries, and he concludes that it is effective, provided the enzyme preparation is given sufficient time to act, the time depending on the temperature. He finds that at 59° F., three days is sufficient; at 48° F., 12–15 days; at 36°–37° F., 30–40 days. More recently Lamsen[119] proposes to utilise the proteoclastic enzymes of the yeast present in a racked beer for rendering the protein permanently soluble. A portion of the freshly racked beer containing yeast is cooled to a temperature (below 26° F.) at which it solidifies, when it is transferred to the main portion of the beer.

C. S. Ash[120] proposes to replace the pasteurising and chilling processes of rendering beer stable and permanently bright by treating it at the time of krausening or carbonating with 35–60 mgms. of tannic acid or the equivalent amount of its salts, and 25–50 mgms. of sulphurous acid or the equivalent of sulphites per litre of beer. The beer is agitated and then allowed to stand until the required changes have occurred, which is usually about ten days. The nitrogenous matters giving rise to turbidity under ordinary circumstances are thus precipitated, and easily removed by filtration before racking into casks and bottles.

A patent has been granted to J. Beerhalter[121] for the production of a non-alcoholic chill-proof beverage. A wort is prepared from malted grain with or without the addition of raw grain, sugar, hops, etc., and to it is added immediately after cooling or at any time before racking or bottling, a proteoclastic enzyme active in slightly acid media. It is claimed that the treated beverage remains bright when pasteurised or chilled.

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[117] Eng. Pat. 2350, 1911; *J.*, 1911, 916, 1027

[118] *Brasserie et Malterie*, 1916, 6, 161; *J.*, 1916, 1170.

[119] U.S. Pat. 1916, 1,177,117; *J.*, 1916, 613.

[120] U.S. Pat. of 1917, 1,234,255; *J.*, 1917, 1059;

[121] U.S. Pat. 1,240,016 of 1917; *J.*, 1917, 1144.

W. A. Steingmann[122] describes a process for producing what he denotes an unfermented malt beverage. According to this process malt is mashed alone or mixed with barley, rice, corn grits, bran, middlings and the like, at a temperature of 116° F. This procedure hydrolyses the proteins. The wort is then filtered from the starch and repeated extractions are made, the wort being finally heated from 95° 158° F. After treatment with hops, etc., it may be fermented or otherwise.

"*Head*"*-producing material.* For the production of a lasting head on fermented beverages, L. Stein[123] claims a preparation made on the following lines. Washed yeast (100 parts) is mixed with gelatin (5 parts), and the mixture is incubated at a temperature not below 100° F. or above 104° F., stirring occasionally. After 72 hours a homogeneous mixture of high viscosity ensues, the transformation being due to the proteoclastic enzymes of the yeast on both the yeast and the gelatin. The mixture is then boiled and evaporated to a syrupy consistency in a vacuum pan.

"*Head*" *retention and hops*.—According to R. Heusz[124] the favourable effect of hops as regards the "head" retention of beer is due to the hop resins. It is interesting to note that mixed malt and hop extracts had a greater and more permanent "head" than had either extract alone. Thus after shaking each extract for two minutes and allowing it to remain for 20 minutes, the ratios of the height of liquid to the height of "head" were as follows: Malt, extract, 1 : 0·36; hop extract, 1 : 0·06; mixed extracts, 1 : 2·38. The author's observations that the filtrates from a boiled sweet wort and from a boiled hop wort contain substantially the same percentage of nitrogen has been explained by H. T. Brown,[125] who shows that the nitrogen contributed to wort boiled with hops is practically equivalent to that precipitated by the hops.

Filter pulp.—W. A. J. Foster[126] gives an historical account of the use of filter pulp in brewing. He points out that since the outbreak of war, this material has been manufactured in our own country and practical results show that it is quite as good as the German make. The pulp should consist of cotton fibre only.

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[122] U.S. Pat. 1,237,724 of 1917; *J.*, 1917, 1143.

[123] U.S. Pat. 1,237,723 of 1917; *J.*, 1917, 1143.

[124] *Zeits. ges. Brauw.*, 1916, **39**, 49; *J.*, 1916, 859.

[125] *J. Inst. Brewing*, 1909, **15**, 222; *J.*, 1909, 134.

[126] *J. Inst. Brewing*, 1916, **22**, 413; *J.*, 1916, 1170.

Use of hydrogen peroxide in the brewery.—H. B. Wooldridge[127] shows that hydrogen peroxide is a valuable bleaching agent and steriliser for treating filter pulp. He also advocates its use for treating foul and fusty casks and screw stoppers and possibly for other purposes in the brewery. As regards so-called stinking casks Wooldridge very properly disclaims the curing of those in an advanced state of decay.

YEAST.

The presence of a well defined vacuole has long been recognised as a criterion of a healthy vigorous yeast for brewing purposes, yet much controversy has arisen as to the physiological significance of the vacuole. The work of H. Wager has done much to clear up this question. In a summary of his researches[128] Wager gives reasons for arriving at the conclusion that the main vacuole of a yeast cell is the nucleus, and that the smaller body adjacent (not within) the vacuole is the nucleolus. To meet the objection to these views that there are sometimes several vacuoles, Wager believes these subsidiary vacuoles to be such within which glycogen is formed. Guilliermond[129] opposed Wager's views on the ground that the presence of volutin (metachromatin)[130] in the vacuoles showed that one of its functions was that of secretion and therefore that it must be placed outside the category of nuclear structure. Wager in refutation of this, however, pointed out that volutin contains nucleic acid and that its elaboration is not at all unlikely to take place within the nucleus. W. Henneberg[131] states that the "vacuole bodies" within the yeast cell contain "volutin drops" and that by staining with methylene blue the volutin usually stains red, whilst the vacuoles themselves stain red, violet, or blue. Henneberg believes that there is a very close connection between the content of volutin and the fermentative power of a yeast. Volutin, he says, may be the mother substance of zymase or it may be the enzyme itself. In the case of mycodermic yeasts volutin may be related to the oxidising activity of the cells. He observed in the case of lactic and acetic bacteria a connection between volutin and the formation of acids.

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[127] *J. Inst. Brewing*, 1916, **22**, 436, *J.*, 1916, 1171.

[128] *J. Inst. Brewing*, 1911, **17**, 2.

[129] *Comptes rend.*, 1910

[130] A. Meyer, *Bot. Zeit.*, 1904, **62**, 113.

[131] *Woch. Brau.*, 1915, **32**, 301, 312, 320, 326, 334, 345, 351; *J.*, 1916, 268.

T. Bokorny[132] shows that yeast weakened by several hours' treatment with an aqueous solution of 0·1 % concentration of formaldehyde, chloroform, phenol, or mercuric chloride, fermented sucrose or maltose more rapidly than dextrose, and he suggests as an explanation that the hexoses formed by the yeast enzymes from the bioses are in the nascent state. Yeast was found to hydrolyse amygdalin, although the hydrogen cyanide formed is toxic, but it is without action on salicin, arbutin, or coniferin.

Fermentation (yeast outcrop).—L. Lindet[133] finds that in fermentation experiments with sucrose and salts, *e.g.*, ammonium sulphate or tartrate, as sources of nitrogen, the conversion of sugar into glycerol, succinic acid and excess CO_2 beyond that required by the Gay Lussac equation, is about 17 times as great as the dry yeast crop. When the solutions contained 2 % of gum arabic, peat humus, or tannin, fermentation was more rapid, the yeast crop was trebled and the fermentation loss was reduced by one third. In fact, with these substances in presence of ammoniacal or amide nitrogen yeast developed almost as rapidly as in media containing proteins. These, it may be added, are laboratory experiments.

Brewery By-Products.

Dried grains.—There are two main reasons for drying spent grains. The first is that in the moist condition they are liable to become convenient substrata for micro-organisms and therefore to undergo putrefaction, and the second is that the cost of the cartage of grains containing 80 % of moisture is necessarily greater than that of grains dried down to 10 % of moisture. But apart from whether the brewer or distiller is able to get at least proportionately more for dried grains as compared with wet when both are calculated to their respective contents of solid matter, the most efficient and economical method of drying should always be adopted. It is obvious that a preliminary removal of a certain quantity of the moisture by pressing is advantageous provided this be not carried so far as to cause the loss of too much of extractive matters. A long discussion on this most important question in which the latest and most economical forms of presses and driers are described s contained in a paper by G. J. Patitz.[134] For details the original nust be consulted.

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[132] *Pfluger's Archiv*, 1916, **164**, 203; *J.*, 1917, 608.

[133] *Comptes rend.*, 1917, **164**, 58; *J.*, 1917, 156.

H. F. E. Hulton and J. L. Baker[135] give the following interesting analyses showing the respective proximate compositions of the total dried grains and of the dust from them.

	Total grains.	Dust.
Moisture	10·3	9·3
Proteins (Nitrogen × 6·25)	18·0	30·2
Total ash	3·8	3·7
Silica (SiO_2) % on total ash	53·0	44·0
Phosphoric acid (P_2O_5) % on total ash	27·0	32·6
Oil	6·5	9·7
Crude fibre ...	17·7	10·7
Pentosans (furfural × 1·8)	27·5	15·1
Assimilable carbohydrates (by difference) including pentosans but excluding fibre	43·7	36·3
Calories per lb. ...	1124	1646

Dried spent hops.—J. L. Baker and H. F. E. Hulton[136] show that the analysis of ground dry spent hops indicates that they are of considerable feeding value, and they are therefore being incorporated with other materials in the preparation of feeding cake, the hops being previously dried down to a moisture content of 1·7 %. Attention is called, however, to the fact that consignments have sometimes heated so much in transit that they fired. It is suggested that the phenomenon originates in an oxidation of the resins. If the hops are spread out in a fairly thin layer for 24 hours before bagging no cases of firing have up to the present been experienced.

Surplus yeast.—Not many years ago, the brewer found considerable difficulty in disposing of his surplus yeast; if washed down the drain it led to septic effluents. In more recent times its value has been recognised and many uses have been found for it. Thus yeast extract is now sold as an article of human dietary. Yeast has also been used as a manure, and finally in a dried condition it is used as a constituent of cattle foods.

As a cattle food dried surplus yeast has been found very useful, and some experiments on this subject are recorded by C. Crowther and H. E. Woodman,[137] who as a result of experiments on sheep arrive at the conclusion that dried yeast must rank with the most highly digestible foods used on the farm.

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[134] Amer. Soc. Brewing Tech., 1916; *J. Inst. Brewing*, 1916, **22**, 247.

[135] *J. Inst. Brewing*, 1917, **23**, 254; *J.*, 1917, 608.

[136] *Ibid.*, 1917, **23**, 455; *J.*, 1918, 103A.

Bakers' yeast.—It is well within the memory of many that brewery yeast was used exclusively for baking, but it was found that a special kind of distillery yeast, which before the war was imported in large quantities from Holland, Belgium, and Germany, as well as produced in this country, is not only quicker in its action in raising the dough, but as it is practically tasteless, it produces that particular kind of bread which finds favour with the public. Since both brewers' and bakers' yeasts belong to the same species, it would seem feasible to find a simple process of transmuting the one into the other. Numerous attempts have not, however, been attended with success. But it may be pointed out that whilst brewery yeasts are only aerated up to an attenuation of half gravity, bakers' (distillery) yeasts are, in many distilleries, aërated more or less throughout the whole operations. J. L. Baker[138] has carried out a number of experiments with brewers' yeast previously washed with a very dilute salt solution and then allowed to ferment briskly in dilute mash tun wort. The experiments were carried out in machine bakeries, and hand bakeries, with one-third brewers' yeast and two-thirds bakers' yeast; with equal parts of brewers' yeast and bakers' yeast; with bakers' yeast alone; and with brewers' yeast alone. The loaves were submitted to two experts, and the results are certainly encouraging. It may be pointed out that C. H. Hoffman[139] finds that the addition of ammonium chloride to the dough before it rises, increases the evolution of gas (though this is not the case when the salt is added to a fermenting solution) and is assimilated by the yeast.

DISTILLING

Commercial alcohol.—The demand for alcohol and other volatile products of fermentation is now very great, but the processes which are being adopted for their production cannot, for obvious reasons, be discussed. One of the cheapest sources of industrial alcohol is molasses Beet molasses, which has not been used in this country for the manufacture of alcohol to any extent for many years, contains under 50%

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[137] *J. Agric. Science*, 1917, **8**, 448.

[138] *J.*, 1917, 836.

[139] *J. Ind. Eng. Chem.*, 1917, **9**, 148; *J.*, 1917, 350.

of sucrose and but a trace of reducing sugar. It yields just over 5 gallons per cwt. of proof spirit. Cane molasses, on the other hand, has for the past 15 years been the chief source of industrial alcohol in this country. That used for distilling contains usually 55–57% of sugars—a mixture of equal parts of sucrose and reducing sugars. The average yield from such molasses is 6¼ gallons of proof spirit per cwt. Questions of freight have restricted the importation of normal quantities of this material during recent years, but there is an abundance of it in cane sugar producing countries, so much so in fact that in some parts of the world its disposal is one of the most difficult problems with which the sugar manufacturer has to deal. Before the war crude manioc flour containing over 70% of starch was available at a price which rendered it an excellent raw material for the production of commercial alcohol. At the present time insufficient is imported to enable it to be used for this purpose. Recently it has been suggested that horse chestnuts and acorns which up to the present have been to a great extent allowed to go to waste—only a small quantity, which principally consisted of the latter, being fed to pigs—should be employed as a source of alcohol. The most recent analyses of these materials by J. L. Baker and H. F. E. Hulton[140] show that peeled horse chestnuts contain 8–17% of sucrose and 15–30% of starch, whilst peeled acorns contain some 40% of starch with a trace of cane sugar (cp. p. 411). The problem of the use of these materials as sources of alcohol is one which has been discussed for many years, but the difficulty which stands in the way of their use is that of their collection.

A paper on the cheap production of alcohol in the United States of America has been published by A. M. Breckler.[141]

An apparatus for the continuous distillation of alcohol is described by A. Chenard.[142]

Potable spirits.—For the preparation of alcoholic liquids of high aroma, particularly Colonial rums, P. M. H. Hervé[143] proposes to distil the fermented wash first in an ordinary still so as to produce a distillate of about 25% strength, the distillate being subsequently redistilled through a rectifying column so that a spirit of about 77% strength is obtained. E. Kayser[144] has conducted experiments to ascertain whether the characteristic differences in the yeasts obtained from rums are manifested when media other than cane products are fermented with them. He fermented cane and beet molasses with a bottom-fermentation yeast and a Schizosaccharomyces, with the result that in both cases the characteristics were preserved. The bottom-fermentation yeast produced seven to ten times as much higher alcohols as the Schizosaccharomyces. The author concludes that by the employment of mixtures of the two yeasts, it might be possible to keep the limits of higher alcohols between 30-300 parts per 100,000 of absolute alcohol in the sample. F. I. Scard[145] gives data for the complete scientific control of a rum distillery.

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[140] *Analyst*, 1917, **42**, 352.

[141] *J. Ind. Eng. Chem.*, 1917, **9**, 612; *J.*, 1917, 902.

[142] Fr. Pat., 480,558 of 1915; *J.*, 1917, 157.

[143] Fr. Pat., 480,601, of 1915; *J.*, 1917, 158.

[144] *Compt. rend.*, 1916, **162**, 647; *J.*, 1916, 612.

In a paper by E. Kayser[146] the results of an examination of the spirit obtained by the fermentation of apple must with *S. mali Risleri* are described. Unlike ordinary cider spirits, the ester content was less than that of higher alcohols, and not very different from the aldehyde content. The content of acids, aldehydes (including furfural), esters, and higher alcohols, ranged from 375 to 618 parts per 100,000 of absolute alcohol.

WINES.

The de-acidification of wines by addition to them of dipotassium tartrate whereby monopotassium tartrate is deposited, first suggested by Liebig, has been studied by T. Paul,[147] who points out that when a saturated solution of the dipotassium salt is added to a wine, the concentration of H·-ions, on which the acid flavour of the wine depends, is reduced immediately, although the separation of tartar may not be complete for 24 hours. In practice, therefore, small quantities of a saturated solution of the dipotassium salt should be added to a wine until the desired alteration in flavour is attained when the wine should be left for the tartar to separate.

L. Laborde,[148] in a study on the causes of the formation of aldehydes in wine concludes that such formation occurs during the storage of young wines in casks in which it is assisted by atmospheric oxygen. The three principal agents which promote the formation of aldehydes under these conditions are the tannin substances more or less combined with potassium hydroxide, oenoxydase, the oxydase of *Botrytis cinerea*. Pasteurisation and the addition of sulphurous acid check the formation of aldehydes. Pasteurisation has a similar effect on wines affected with *casse*, but in such wines sulphurous acid promotes the formation of aldehydes. Complete disappearance of aldehydes may occur when wines are stored in absence of air (in bottles ?). The formation of aldehydes as opposed to their destruction is evanescent, although it always impairs the bouquet of red wines in casks. It is pointed out that facultative aërobes such as mycodermæ produce aldehydes, although some anaërobes help to remove the aldehydes unless the wines contain sulphurous acid. The same author had previously published an account of a long investigation on the rôle of sulphurous acid in wines.[149] When added to wine to the extent of 100-200 parts per 100,000, most of the sulphurous acid enters into combination with dextrose but not with lævulose. The antiseptic value of combined sulphurous acid is greatly reduced, but in this condition it can modify the action of the yeast.

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[145] *Int. Sugar J.*, 1916, **18**, 493; *J.*, 1917, 157.

[146] *Bull. Soc. Agric. France*, 1916, 262; *J.*, 1917, 902

[147] *Zeits. Elektrochem.*, 1917, **23**, 65; *J.*, 1917, 561

[148] *Ann. Inst. Pasteur*, 1917, **31**, 215; *J.*, 1917, 1107.

Fonzes-Diacon[150] points out that the addition of 0·5 grm. per litre of citric acid (the legal limit in France) to white wines does not always prevent the occurrence of *casse*.

F. Kayser[151] finds that the addition to grape must of 1 to 1·7 % of nitrogenous substances in the form of ammonium sulphate, asparagine, and ammonium phosphate increases the formation of esters in most cases during fermentation, ammonium sulphate being usually of less effect than the other substances.

CIDER.

O. Grove[152] has examined between 30 and 40 acetified samples of cider and isolated five different types of bacteria. The most common species was the *Bacterium xylinum*. The conclusions drawn from this investigation are that acetic bacteria are invariably present in ciders made under ordinary conditions and that acetification will occur during storage in cask unless special precautions are taken. The simplest of these appears to be to cover the surface of the liquor with a layer of tasteless liquid paraffin, at least a quarter of an inch in depth. Somewhat less efficient was found to be the charging of the cider with carbon dioxide. The suggestion is thrown out that by encouraging a slight lactic acid fermentation, acetification and perhaps also sickness and ropiness may be kept under control without impairing the flavour of the cider. This problem is under investigation

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[149] *Rev. Viticulture*, 1916, **45**, 309, 373, 421, 437, 453; *J.*, 1917, 935.

[150] *Comptes Rend.*, 1917, **164**, 650; *J.*, 1917, 561.

[151] *Rev. Viticulture*, 1916, **45**, 149, 165; *J.*, 1917, 902.

[152] *Annual Report of Agric. and Hortic. Research Station*, Long Ashton, Bristol; *J. Oper. Brewers' Guild*, 1916, **3**, 124, 150; *J.*, 1916, 191.

VINEGAR.

An important paper on this subject is that by C. A. Mitchell.[153] The author's experience leads him to adopt a process of mashing with a malt of diastatic power about 80 (Lintner) in which the initial temperature is about 120° F. The rakes are started and the mash temperature raised slowly to 150° F. by the admission of naked steam below the false bottom of the tun. After making a second mash on these lines, the goods are sparged with water at about 155° F. the final runnings have a specific gravity of 1005 1008. High pitching temperatures are employed and with some yeasts the temperature may be 72° to 74° F. With a good diastatic malt a wort of 1055 should attenuate to 1001. Fermentation is complete on the third day when the gyle is allowed to stand for a few days during which period it becomes sour owing to infection with vinegar bacteria. This preliminary souring saves time in the acetifiers, and removes the young yeast which interferes with the subsequent acetifying. The essential conditions for acetifying are the presence of acetic bacteria and a sufficient supply of air. The author believes that of the numerous acetic bacteria described, some are only modifications. That of most common occurrence in this country is the *Bacterium xylinum* of A. J. Brown[154].

A volatile reducing substance, $CH_3 \cdot CHOH \cdot COCH_3$, acetylmethylcarbinol, is shown by R. W. Balcorn[155] to be a normal constituent of cider vinegar. L. M. Tolman[156], has studied the changes undergone by cider during fermentation, prolonged storage, and conversion into vinegar. Vinegar made in New York in rotating generators had the composition acetic acid 6·6 %, alcohol 0·25 %, total solids 1·24 %, ash 0·32 %. The yield was 170 gallons per ton of apples. Much of the malic acid is converted into lactic acid during fermentation, the remainder being oxidised during acetification.

RÔLE OF ALCOHOLIC LIQUORS IN HUMAN DIETARY.

The question of the dietetic value of spirits, wines, and beers is a very thorny one, dividing as it does physiologists into opposite camps, quite apart from prejudiced interested parties who take one side or the other without basing their judgments on scientific data. One of the chief points of the problem is the question of the physiological effects of alcohol itself. Naturally it would be beyond the scope of this Report to deal exhaustively with this problem, and contemporary views thereon only can be cited. Thus it may be pointed out that Professor Bayliss, in his little work recently published, "The Physiology of Food and Economy in Diet" (Longmans, Green & Co., 1916), deplores the fact that some temperance advocates have done harm to their cause by making statements which their opponents are able to disprove, one being the denial that alcohol is in any sense a food. He agrees that alcohol is burnt up in the body and that it has a very high energy value, yet he characterises it as a narcotic and states that its supposed stimulating action is explained by the fact that it paralyses the inhibiting mechanism, and not because it excites activity of a true stimulating action. Now let us take the views of another eminent writer, Sir James Crichton Browne, who supports the other side. Writing in a pamphlet published by the True Temperance Association, under the title of "What we Owe to Alcohol," Sir James points out that the public are told *ex cathedra* that the *use* not the *abuse* of alcohol leads to troubles in the system. It is obvious that every article of diet can be abused. He draws attention to the well-known fact that small quantities of alcohol are formed in the tissues of vegetables and animals.[157] Finally, in a summary of his pamphlet, he urges that the benefits which the human race have derived from alcohol far outweigh the evils which have arisen from its abuse.

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[153] *J. Inst. Brewing*, 1917, **23**, 357 ; *J.*, 1917, 1244.

[154] *J. Chem. Soc. Trans.*, 1886, **39**, 439.

[155] *J. Amer. Chem. Soc.*, 1917, **39**, 309 , *J.*, 1917, 350.

[156] *J. Ind. Eng. Chem.*, 1917, **9**, 759 ; *J.*, 1917, 1024.

Now to come to wines and beers, no one can deny the useful stimulating effects in certain circumstances of these drinks. But to claim for them a high position as flesh-forming foods is clearly wrong. Dealing more particularly with beers, certain of the laity have avowed that they are flesh-forming foods, and they argue that because the proteins of the grain are highly digested (in the sense of being broken down), by the effects of the malting and brewing processes, beers are *ipso factô* digestible flesh formers. In reality we know that only a small portion of the nitrogenous substances present in beer are flesh formers, and if we accept the values recently published by J. S. Sharp (*see* p. 117), whose results it must be admitted do not err in being on the high side, nothing but a minute trace of the nitrogenous substances in beer exists as true proteins. But none the less, beers, whilst they cannot be regarded as flesh formers, are valuable articles of dietary, and are actual foods in the sense of being fuels. A writer in the *Lancet* (September 15, 1917) has, in the opinion of the writer of this Report, put the dietetic value of beer in the right light, which is substantially that just enunciated. Beers are known to contain a number of enzymes, probably rendering them valuable digestive agents when consumed with other foods. They also probably contain those accessory agents known as vitamines, which have been shown to be present in yeast.[158]

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[157] In their report to the House of Commons in 1806, Drs. Hope, Coventry, and Thomson state that if some of the steeped malt which has acquired the odour of apples be taken at the early stages of germination on the malting floor, and distilled in a steam bath, "a little spirits will be found in the liquid which comes over." Pasteur found that, if certain fruits were placed in an atmosphere of corbon dioxide, the sugar diminished in quantity, owing to the occurrence of alcoholic fermentation by the internal cells. Pasteur estimated the amount of alcohol formed and demonstrated the absence of yeast in these experiments. In more recent years J. Stoklasa and F. Czerny (*Ber.* 1903, **36**, 4058; *J.*, 1904, 38) have observed that zymase, the enzyme of alcoholic fermentation, is present in the freshly expressed juices from the tissues of some organs of the higher animals and plants. Zymase has also been shown to be present in ripe sugar beets and in stored potatoes by J. Bodnar (*Math. és Termés. Ertesito*, Budapest, 1915, **33**, 591; *J.*, 1917, 97).

The question now arises in view of what has been said? Is it wasteful to make barley into beer? If barley could be consumed as a human food, then it would be more economical to use it in that way than to make it into malt and beer, which processes involve losses. But barley is a cereal which is not used largely as a human food, *e.g.*, for bread making it is unsuitable, except when mixed with a large proportion of wheat. Moreover, when fed direct to animals, the main return in the form of flesh is from a portion of the proteins. The starch and other carbohydrates are completely burnt up, giving the animal body heat, and hence except for this they are completely lost. When made into beer, on the other hand, not only are starch and other carbohydrates *not* completely burnt up, but the alcohol which results from them to the extent of 50 % of their weight has a very high fuel value. Thus it is a most efficient source of energy as it is rapidly and completely burnt up in the system. The reader is referred in this connection to a portion of a "Report" drawn up by a Committee of the Royal Society at the request of the President of the Board of Trade, dated December 9, 1916, entitled :—"*A consideration of the Economy which might be effected by the Prohibition of Brewing.*"[159]

Thus is brought to a conclusion a brief summary of progress in a branch of industry of wide and far-reaching importance. That researches conducted in the fermentation industries are not only of benefit to the industries themselves, but that they also contribute to the general welfare of mankind, is as true to-day as it was in the time of Pasteur. It is therefore remarkable that some of those engaged in these industries, from whose ranks have been recruited many of our leading scientific thinkers, have been tardy in recognising the true value of science. They have, as Dr. H. T. Brown pointed out recently, "been content to go on either in total ignorance of principles . . . or with but a mere smattering of so-called scientific knowledge, picked up anyhow, having no real educational value, and often worse than useless." But—"*Tempora mutantur.*" The necessity of keeping *au courant* with science is now generally recognised. Is it not a sign of the times that the Institute of Brewing has decided to grant a diploma to brewers, distillers and maltsters who have satisfied a board of examiners that they have received adequate training in the principles and practice of those branches of technology appertaining to their daily work? The days of blind empiricism have, we may hope, gone, never to return.

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[158] *Cp.* A. Seidell, *J. Biol. Chem.*, 1917, **29**, 145; *J.*, 1917, 562.

[159] *J.*, 1917, 198; *cp.* also M. Buremann, *Zeits. ges. Brauw.*, 1916, **39**, 331; *J.*, 1917, 899.

Since the commencement of the present year, when this Report was written, certain further restrictions of brewing have been imposed. Under an Order by the Food Controller dated March 19th, 1918, entitled "The Intoxicating Liquor (Output and Delivery) Order, 1918," a brewer is not allowed to brew in any quarter beer of an original gravity below 1010. Further, the average original gravity of all beer brewed by him during any quarter (other than beer brewed under any licence granted by or under the authority of the Food Controller specially stating the gravity at which the beer brewed thereunder is to be brewed) may not exceed 1030 in the case of the United Kingdom, or 1045 in the case of Ireland. To give facilities to brewers for yeast production provision is made by the order to allow beer to be diluted with water, which dilution must be carried out in a gauged vessel.

WATER PURIFICATION AND SANITATION.

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Water.

A considerable amount of work has been carried out in connection with the temporary purification of water for the moving armies in the field. No novel processes have been introduced, and the Sanitary Authorities responsible for supplying water have been content to adapt known processes to their needs. The method of purification most generally used is the chlorine process, in which the free chlorine is obtained either from hypochlorites or from liquid chlorine compressed in cylinders. The method, though simple, requires to be kept under control, and it is in maintaining this control that new processes have had to be found. As ordinarily applied, the method consists of adding excess of a solution containing the free chlorine to the water to be purified, allowing the mixture to stand for a certain length of time and then destroying the excess of chlorine added. The details of the actual plants used during the year have not yet been officially disclosed. In London, according to Houston, the adoption of chlorine sterilisation has saved the Metropolitan Water Board £11,167 in coal during the short period of its use.

As one would expect, the amounts of chlorine required by different waters vary considerably, so that preliminary trials have to be made. According to Guillaume and Vienne[1] the absorption of active chlorine varies with the dose and the time. The treatment is allowed to go on, but speaking generally, the absorption is constant when 50 mgrms. per litre of chlorine is allowed to act for six hours. This constant has been termed the "coefficient of absorption of chlorine." The constant is naturally decreased if the water under treatment has already been treated, and tests have to be applied to ascertain if such is the case. The nitroso-indol test for nitrites will show if chlorine as chlorine has been used for the chlorination, since nitrites are produced by the process, but if hypochlorites have been used, nitrites are not produced, and one must rely on the actual determination of the absorption coefficient of the water and compare it with the coefficient of similar water not so treated. The coefficient is determined by adding hypochlorite of known strength to a definite volume of water, allowing the mixture to stand over-night, and then adding an iodide, acetic acid, and excess of thiosulphate. From the excess of thiosulphate used, determined by titration with iodine, and the quantities added, the required constant can be calculated. A check on the figures is obtained by determining the oxygen absorbed from permanganate, which should be lower with the water that is suspected of having been treated. For practical purposes the excess of chlorine used is removed by thiosulphate, for the presence of which in waters two methods of detection and estimation are given by Golse.[2] In the first of these methods the water is treated with silver nitrate; the silver chloride precipitated is dissolved by ammonia and if any thiosulphate was present in the water, a brown turbidity due to the formation of silver sulphide with the thiosulphate is obtained. The amount of this can be estimated colorimetrically with standard thiosulphate and silver nitrate. In the second and more sensitive method, a known volume of water is mixed with potassium iodide solution (5 %) and hydrochloric acid (1 in 10) and a small amount of benzene sufficient to form a thin layer at the top. On the gradual addition of standard potassium iodate, iodine is produced which is absorbed by the thiosulphate. Addition of the thiosulphate is continued till a slight reddish tint can be seen on the benzene film. The amount of iodate required is a measure of the thiosulphate in the water.

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[1] *J. Pharm. Chim.*, 1915, **12**, 377; *J.*, 1916, 66.

Occasionally the excess of chlorine added is not reduced by thiosulphate but allowed to dissipate of its own accord, or sulphite or gaseous sulphur dioxide is added. In such cases it is necessary to be able to detect the amount that is present. The usual process for detecting free chlorine by starch iodide solution is sensitive to 1 in 10 millions. For more dilute solutions of free chlorine, Le Roy[3] uses a few drops of a solution of hexamethyl-tri-*p*-aminotriphenylmethane which produces a violet coloration varying in intensity according to the free chlorine present. The solution is prepared by dissolving one part of this compound in dilute hydrochloric acid (1 : 1) and making up to 100 c.c. with distilled water. A little formic or acetic acid is added to prevent any opalescence which some natural waters are prone to give. The reagent is unaffected by hydrogen peroxide, but works slowly in the presence of nitrites. It can detect three parts of chlorine in 100 millions. According to Ferrand[4] the excess of free chlorine present in waters treated with hypochlorite can be removed by hydrogen peroxide with results better than those attained with thiosulphate.

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[2] *J. Pharm. Chim.*, 1916, **14**, 8; *J.*, 1916, 862.

[3] *Comptes rend.*, 1916, **163**, 226; *J.*, 1916, 976.

In connection with the above method of purifying water, the modification suggested by J. Race[5] is worthy of mention. Here ammonia is used in conjunction with hypochlorite and the resulting ammonium hypochlorite which is formed by double decomposition, when tested with *B. coli*, is found to be 20 or 30 times stronger than a solution of calcium hypochlorite containing the same amount of available chlorine. The high germicidal power of ammonium hypochlorite is attributed to the presence in the solution of chloramine, NH_2Cl, which is produced by the spontaneous decomposition of the ammonium hypochlorite thus:—$NH_4ClO = NH_2Cl + H_2O$. Chloramine is known to have a much greater germicidal value than its equivalent of chlorine and to be produced by the action of ammonia on bleach. Further, when the ammonium hypochlorite is used there is practically no absorption of the available chlorine. Thus, tests carried out at Ottawa with 10 parts of available chlorine per million, gave an absorption of about 60% of the available chlorine after an hour's contact when bleaching powder was used, but only 3% when ammonium hypochlorite was used. The process has not yet been applied on a large scale. Ammonia has not the same intensifying action when added to chlorine water or when chlorine gas from cylinders is used for water sterilisation.

Amongst the novel forms of water purification, the method of Linden[6] is worthy of special mention as it appeals to the general public and to those authorities who have in the past been opposed to the addition of chemicals to water. In this method the water is agitated violently in a receptacle or series of receptacles, so that every article of the water undergoes agitation. It is claimed that the water, is completely sterilised in a few minutes. The water may be saturated with air before being agitated. In the more recent patent a filtering material is introduced through which the agitated water has to pass before being ready for use. A portable form of the apparatus can be mounted on a motor vehicle, and the motor of the vehicle used to supply the power for working the apparatus. Further experimental details with this method of sterilisation by bombardment or impact are required.

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[4] *Comptes rend.*, 1916, **162**, 438–440; *J.*, 1916, 485.

[5] *Lancet*, July 8, 1916; *J.*, 1916, 904.

[6] Fr. Pat. 478797, 1914, and Eng. Pat. 104710, 1916; *J.*, 1916, 1129; 1917, 1106.

A new organic substance for the sterilisation of water is *p*-sulpho-dichloraminobenzoic acid, which Dakin and Dunham[7] have shown owes its germicidal value to the NH_2Cl group. The compound, which has the formula $ClNSO_2C_6H_4COOH$, is also known under the name "Halozone," and is obtained from *p*-toluenesulphonic amide, by the action of ammonia on the acid chloride. The amide is first oxidised to *p*-toluenesulphaminobenzoic acid, and this on suitable treatment with chlorine is converted into the dichloramino-compound. The disinfectant may be made into tablets weighing about 0·1 grm., containing 4% of the substance and 4% of sodium carbonate, the remainder being sodium chloride. One tablet is sufficient to sterilise one litre of water, though more may be required when contamination is excessive. These tablets have been adopted by the Navy for use by officers and men serving ashore.

Most of the remaining literature on the subject is concerned with the modification and better adaptation of processes already known.

Horner[8] proposes to purify water by treating it with a mixture obtained by treating bauxite with sulphuric acid. The mixture, which contains basic aluminium sulphate, sulphuric acid, and the solid impurities in the bauxite, splits up when added to the water into aluminium hydroxide, which settles out, entrapping the impurities of the water and those initially present in the bauxite.

For the removal of iron from well water by atmospheric oxygen, Zollner[9] makes the water flow in a shallow stream through a series of conversion channels which contain gravel. The air entrapped in the gravel oxidises the soluble ferrous salt to insoluble ferric compounds which are then carried in suspension by the water into a sludge chamber, from which the water filters upwards through a sand filter into a reservoir In another form of apparatus air is supplied in a closed apparatus to which it is led by passing through glass vessels filled with water so that the flow can be observed.

According to the Deutsche Filter Co.,[10] iron and manganese can also be removed from water by adding a small quantity of permanganate (0·0003%) and filtering through a porous catalytic material such as trachytic tuff, whereby the iron and manganese are precipitated. The precipitated oxides are left on the filter and increase the catalytic action.

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[7] *Brit. Med. J.*, 1917, 382; *J.*, 1917, 610; also Adams, *Brit. Med. J.*, Aug. 11, 1917.

[8] U.S. Pat. 1197128, 1916; *J.*, 1916, 1022.

[9] Ger. Pat. 286295, 1913; *J.*, 1916, 196.

[10] Eng. Pat. 405, 1915, *J.*, 1916, 336.

Klut[11] removes iron and manganese by adding alum to the water. The treated water then flows over weirs into settling tanks from which the clear water is pumped through gravel filters to remove iron compounds. Manganese compounds are then removed by passing the water through manganese permutite filters, which are regenerated from time to time by means of 2% potassium permanganate solution. The treatment diminishes the total quantity of organic matter besides removing iron and manganese, and does not increase the hardness. Subsequent filtration through permutite filters containing marble removes any free dissolved carbon dioxide.

For the purification of water containing iron in organic combination, W. Wagenknecht[12] mixes the water to be purified with water containing iron in inorganic combination and treats the mixture with a quantity of lime water equivalent to the inorganic iron. The mixture is then passed over a trickling filter. The colloidal ferrous hydroxide first formed is oxidised to ferric hydroxide, then precipitated, carrying down with it the iron in organic combination.

For removing gases absorbed in water, C. Hülsmeyer[13] filters water from the bottom upwards through a layer of turnings or shavings of suitable material or through a bed of fibrous material such as hemp or horsehair. The receptacle through which the water is filtered is funnel shaped, and has a distributing plate having openings increasing in size from the centre upwards towards the periphery. The water is drawn off by an outlet pipe which extends below the surface of the water, and is provided with a plate which prevents the liberated gases from entering the pipe.

Oxygen may be removed from water[14] by treating it with sodium sulphite, and then filtering through a porous inorganic material impregnated with an oxide, especially cobalt oxide, capable of exerting catalytic action.

Several new modifications in the methods for water analysis have been described. O. Mayer[15] has modified Wartha's acidimetric method for determining the hardness as follows:—*Temporary hardness.*—200 c.c. of water is boiled for 30 minutes, cooled, diluted to original volume, and filtered. The precipitate, together with 10 c.c. of the liquid, is titrated with *N*/10 hydrochloric acid and methyl orange.

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[11] *Mitt. K. Land. Wasserhyg.*, 1916, **21**, 262; *J.*, 1917, 99.

[12] Ger. Pat. 294098, 1913; *J.*, 1916, 1176.

[13] Ger. Pat. 288158, 1913; *J.*, 1916, 435.

[14] Permutit A.-G., Ger. Pat. 288488, 1914; *J.*, 1916, 435.

[15] *Z. anal. Chem.* 1915, **54**, 289; *J.*, 1916, 272.

Allowance is made for the alkalinity of the 10 c.c. of liquid if this should be alkaline. Generally the alkalinity is due to magnesium carbonate, but alkali carbonates may also be present. These may be detected by evaporating the water to dryness and treating the residue with 60% alcohol and phenolphthalein. They may be estimated by evaporating a litre of the water and extracting the residue with dilute alcohol till the extract is no longer alkaline. The alcohol is then evaporated to dryness, and the aqueous solution containing only alkali carbonates is titrated with acid and methyl orange. The *total hardness* is determined on 200 c.c. of water boiled with the "alkali mixture" containing 20 grms. of sodium hydroxide and 30 grms. of sodium carbonate per litre, and the precipitate formed after washing with 70% alcohol is titrated with acid.

Another modification of the same process by Kay and Newlands[16] is as follows: 100 c.c. of water is mixed with 10 c.c. of $N/25$ potassium carbonate (if permanent hardness is believed to exceed 15°, more potassium carbonate is used), the mixture evaporated to dryness on a steam bath, the residue treated with 10 c.c. of 20% alcohol, warmed on a steam bath, and filtered into a flask of resistant glass. The basin is rinsed four times with 5 c.c. of cold 90% alcohol, the liquid filtered, and the filter washed five times with alcohol of the same strength, using 5 c.c. each time. The filtrate is titrated with $N/50$ hydrochloric acid, using methyl orange as indicator. The difference between the amount of carbonate added to the water and that found in the filtrate is equal to the permanent hardness. The precipitate on the filter, which consists of calcium and magnesium carbonates, is then dissolved in excess of $N/10$ hydrochloric acid (5 or 10 c.c.), passed hot through the filter, the filter washed with boiling water, and the excess of acid in the filtrate titrated with $N/50$ baryta solution. This gives total hardness. The difference between the total and permanent hardness is temporary hardness. The following precautions are worthy of note:—

(1) During evaporation on the steam bath, contact with oxides of sulphur from coal gas flames or other impurities in the atmosphere of the laboratory must be avoided.

(2) The diluted alcohol must be prepared from absolute alcohol, not from rectified spirit, which is usually acid.

(3) Soft glass vessels must be avoided, only porcelain vessels or vessels made of resistant glass being used.

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[16] *J.*, 1916, 445.

The same authors[17] base a method of separation and estimation of calcium and magnesium on the fact that magnesium carbonate dissolves in excess of ammonium carbonate, whereas calcium carbonate is practically insoluble. It is carried out thus: (a) Total hardness is determined by the method just described (b) The hardness due to calcium salts alone is determined thus: To 100 c.c. of water in a platinum dish 10 c.c. of 2% ammonium carbonate solution (2 grms. of solid and 1 c.c. of concentrated ammonia in 100 c.c.) is added, and the liquid evaporated to dryness on a steam bath; 15 c.c. of the same ammonium carbonate solution is added to the basin, and brought in contact with the whole of the residue, and the mixture warmed on the bath for two minutes and then filtered, retaining as much as possible of the undissolved residue in the basin The extraction is repeated twice with 10 c.c. of ammonium carbonate solution, the dish washed with 90% alcohol, the liquid filtered, and the filter washed with the same alcohol till free from alkali. The calcium carbonate, which now alone remains in the basin, is dissolved in a measured volume of $N/10$ hydrochloric acid, and the excess acid titrated with $N/50$ baryta. The amount of calcium in the water is calculated as degrees of hardness and subtracted from the total hardness, also in degrees of hardness The difference is the amount of magnesium in the water in degrees of hardness

M. Tilgner[18] titrates the water with acid (as in Blacker's method for temporary hardness) and the residual carbon dioxide, which is difficult to expel by a current of air, is neutralised with $N/10$ potassium hydroxide and phenolphthalein prior to the titration with potassium palmitate.

E. B Jensen[19] gives two methods for the volumetric determination of magnesium in mineral waters.

(1) The magnesium, after the removal of calcium, is precipitated as ammonium magnesium arsenate, filtered, and washed with dilute ammonia and then 50% alcohol The precipitate is dissolved in a known quantity of $N/10$ hydrochloric acid and the excess acid titrated with sodium carbonate solution using methyl orange as indicator. The quantity of magnesium present is calculated from the volume of hydrochloric acid neutralised by the precipitate, $MgNH_4AsO_4 + 2HCl = MgCl_2 + NH_4H_2AsO_4$

(2) In this method the magnesium ammonium arsenate is digested with sulphurous acid for two hours, to reduce arsenate to arsenite,

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[17] *J*, 1916, 448

[18] *Chem.-Zeit.*, 1916, **40**, 675; *J*, 1916, 976

[19] *Proc. Australasian Inst. Min. Eng*, 1916, 75; *J* 1916, 1032.

boiled to expel sulphur dioxide, cooled, neutralised with sodium hydroxide and phenolphthalein, rendered acid with tartaric acid, treated with an excess of sodium bicarbonate, and titrated with standard iodine solution. 1 c.c. of iodine ($N/10$) = 0·0012 grm. magnesium. Both methods are stated to yield accurate results.

F. W. Bruckmiller[20] proposes, after the removal of the calcium by precipitation, to treat the solution for magnesium thus :—(1) The solution is evaporated to dryness and the ammonium salts decomposed by heating. The residue is dissolved in a small quantity of water acidified with hydrochloric acid, and after filtering, made slightly alkaline with ammonia. Microcosmic salt is slowly added to the cold solution, with stirring, and after the precipitate has formed, a quantity of ammonia is added equal to one-third of the total volume and the solution allowed to stand for 18 hours. The precipitate is filtered by the aid of suction, and washed with 25 c.c. of alcohol. After transferring to a beaker with hot water, a known excess of $N/10$ hydrochloric acid is added and the excess titrated back with $N/10$ sodium hydroxide, using methyl orange as indicator.

(2) The solution is freed from ammonium salts by evaporation and ignition, the residue dissolved in a small quantity of hydrochloric acid and the solution filtered. The solution is cooled, made alkaline with ammonia solution—free from ammonium salts and an excess of 10 c.c added. A 10 20% excess of sodium arsenate is added slowly, with vigorous stirring, which is continued for 10 minutes after no further precipitation has taken place. The solution is allowed to stand in a cool place to allow the precipitate of magnesium arsenate to settle, and after filtering and washing with 5% ammonia water, the precipitate is dissolved in hot water, and 10 c.c. of concentrated hydrochloric acid and 0·3 grm. of potassium iodide added for every 100 c.c of liquid. The liberated iodine is titrated with $N/10$ thiosulphate.

(3) The precipitate of magnesium ammonium arsenate, obtained as in (2), after washing with dilute ammonia, is dissolved in hot water and the solution transferred to an Erlenmeyer flask fitted with a trap. An excess of iodine and 10 c.c. of sulphuric acid (1 : 1) are added, and the whole boiled rapidly until iodine vapours are no longer visible. While still hot the trace of iodine remaining is destroyed with sulphurous acid, and the whole cooled quickly. The acid solution is neutralised with $N/10$ sodium hydroxide, using phenolphthalein as indicator, and adding

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[20] *J. Amer. Chem. Soc*, 1917, **39**, 610; *J*, 1917, 563.

from time to time a solution of sodium phosphate. When titration is complete the volume of phosphate solution added should be equal to one-half the volume of iodine solution. The arsenious acid is titrated as usual with N/10 iodine.

According to L. W. Winkler[21] small quantities of hydrogen sulphide in water may be determined colorimetrically, larger quantities thus:—The water is collected in a stoppered bottle containing 10 to 20 grms. of marble previously washed with dilute hydrochloric acid. The stopper is removed and replaced by another, carrying a bulb tube, a side tube from which leads first to a U-tube containing cotton wool, and then to an absorption bulb containing 50 c.c. of freshly-made bromine water free from acid. The upper end of the bulb tube is fitted with a separating funnel holding 50 c.c. of 18% hydrochloric acid. The acid is discharged in three quantities—one-half to start with, one-fourth after the lapse of an hour, and the remainder after the lapse of another hour. The hydrogen sulphide is oxidised to sulphuric acid by the bromine, and after evaporating until the bromine and hydrobromic acid are expelled, the sulphuric acid is titrated with *N*/100 borax, using methyl orange as indicator, or preferably the bromine alone may be expelled by boiling and the mixed hydrobromic and sulphuric acid titrated with borax.

Another method has been described by G. Incze.[22] To 300 c.c. of water is added 3 c.c. of a solution containing 85 grms. of silver nitrate and 200 grms. of ammonium nitrate in a total bulk of 500 c.c. In the presence of ammonium nitrate no silver carbonate is deposited, the precipitate consisting of silver chloride and silver sulphide. The excess of silver is measured by allowing the precipitate to settle for an hour, and then titrating 100 c.c. of the clear liquid with *N*/50 ammonium thiocyanate. By performing a parallel experiment with water from which the hydrogen sulphide has been expelled by boiling, the quantity of silver nitrate and the chloride can be ascertained and then, by difference, the hydrogen sulphide.

In the colorimetric determination of nitrates in water in presence of chlorides[23] a loss of the nitrate is caused when the water is evaporated to dryness. By adding sulphuric acid to the aqueous solution complete evaporation of the solution may be obviated. The method is then carried out thus:—

About 50 c.c. of the water (containing 1–5 parts of nitrate per million) is treated with 1·5 c.c. of strong sulphuric acid with constant stirring, and then with 2 c.c. of the phenoldisulphonic acid reagent, the liquid being concentrated first on a water bath and finally at a temperature not exceeding 70° C., to a quantity of 6 or 7 to 12 or 14 c.c. according to the amount of nitrate present. When concentrated thus, the liquid is pale yellow, not dark or turbid. It is then diluted with about 50 c.c. of water, neutralised with alkali and the colour compared with a standard, made by the same process.

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[21] *Z. angew. Chem.*, 1916, **29**, 383; *J.*, 1916, 1176.

[22] *Z. anal. Chem.*, 1917, **56**, 308; *J.*, 1917, 938.

[23] W. F. Gericke, *J. Ind. Eng. Chem.*, 1917, **9**, 585; *J.*, 1917, 904.

Another difficulty experienced when this method is used in the presence of large quantities of magnesium salts is that when the excess of phenolsulphonic acid is neutralised, hydroxides of magnesium and iron, if present, are precipitated and must be filtered off before the colorimetric comparison is made. In the absence of iron the filtration can be avoided by adding excess of ammonium salts.[24] The excess must be larger if sodium or potassium hydroxide has been used in the neutralisation.

The review for the year would be incomplete if it failed to mention the opening of the largest reservoir and aqueduct now in existence—the Ashokan reservoir on Esopus Creek, which supplies the city of New York with a minimum of 250 million gallons of water per day. The Catskill mountain water supply scheme was begun in 1907, and when completed will furnish 500 million gallons a day. The reservoirs collect the water on the Catskill mountains and carry it through tunnelled rock, mountain gorges, and broad plains for a distance of 120 miles to its destination. The portion of the great project which has been completed constitutes only three-quarters of the whole, and embraces the Ashokan reservoir, an artificial lake 12 miles long and 1 mile wide, with an available capacity of 128,000 million gallons, and the Catskill aqueduct, which extends 92 miles from the reservoir to the city's northern boundary and 35 miles within the city's limits. With the development of the second Catskill watershed at Schoharie Creek, the quantity of new water which will be brought to the city will be doubled. The water supply works by the gravity system, *i.e.*, without pumping, and flows from gathering grounds from a much higher elevation than the city. The total area of the gathering grounds and watersheds is 571 square miles, which are very sparsely settled, and the rocks, which are almost wholly sandstones and shales, keep the water unusually soft and free from pollution.

For protecting the quality of the water huge aerators in the form of great fountain basins 500 feet long and 250 feet wide, and containing about 1600 nozzles, so designed that the water is divided into a fine spray, permit the water to be thoroughly aerated and undesirable gases and odours removed. In a few places where, under conditions of storm, the rapid flow of the water may sometimes carry very fine earth along with it, coagulating plants to correct the turbidity so formed, have been installed. To destroy any bacteria the water is chlorinated with chlorine supplied to the water from cylinders by specially designed injectors. Provision has also been made for filtration wherever this is necessary, and the water in the reservoirs can be drawn from depths at which it is in the best condition at any time. Special precautions have been taken to prevent pollution of the streams in the watershed, and an elaborate scheme for destroying timber and vegetable organic matter before filling the reservoir was adopted with a view to diminishing the colour of the bottom waters of the reservoir, and preserving its oxygen content from the commencement of the service.

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[24] M. S. Nichols, *J. Ind. Eng. Chem.*, 1917, 9, 586; *J.*, 1917, 904.

Diénert and Gizolme have continued their study of the chemical changes due to the diatoms present in the surface film of the sand filters at Ivry.[25] When the waters are troubled the diatoms are in suspension and evolve gas containing 60% of oxygen until they finally sink on to the filter bed and add to the effectiveness of its film. The bacterial purification thus varies with the activity of the filter diatoms, and these with the weather, light, temperature, time of day, and season of the year.

The same authors observe[26] that the reduction of the alkalinity of a water during its passage through an open sand filter, owing to the action of algæ, is a direct measure of the purifying power of the filter. Thus, for instance, when the alkalinity has been reduced by about 4 mgrms. of calcium carbonate per litre, *B. coli* disappear from the water, and the total number of organisms present is reduced by about 85%.

For the destruction of algal growths, and to keep water free from weeds in water reservoirs, G. Embrey[27] has given a review of his experience with the use of copper salts at Gloucester. He states that one part of copper sulphate per three million parts of water is sufficient and the amount has no injurious effect on fishes. The number of bacteria present increases shortly after the addition of copper sulphate but then decreases—the increase appearing to be due to the decomposition of the algæ. The sterilising effect upon sewage of acid copper sulphate waste liquors from a munitions factory has been noticed at Newhaven, U.S.A The effect was greatest in hot weather when the bacterial development is at a maximum. To remove the taste imparted to waters by algal growths, A. C. Houston[28] adds potassium permanganate in quantities of 2·5 to 5 lb. per million gallons. The method works better than hypochlorites, and has been tried successfully in reservoirs under the control of the Metropolitan Water Board. For the various methods of softening water, with a critical discussion on their merits see *J.*, August 31st, 1917, p. 911.

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[25] *Comptes rend.*, 1915, 313, J., 1916, 127.

[26] *Comptes rend.*, 1916, **163**, 127, *J.*, 1916, 940.

[27] *Analyst*, 1917, **42**, 264, *J.*, 1917, 977.

SEWAGE.

A distinct advance in the practice of sewage purification has been made by G T P. Tatham,[29] who from practical and theoretical considerations has expressed in mathematical form the relations which the various factors concerned in the purification of sewage bear to one another. The purification which any filter, working biologically, can bring about is dependent on the average time, T, that a drop of liquid remains in contact with the filtering medium, on the rate of flow, F, in gallons per unit time, and also on a constant, L, which varies with the kind of sewage and method of purification. T can be determined by the addition of salt and examining the effluent for salt at regular intervals from the time of application, F can be easily obtained, hence if P represents the amount of pollution in the final effluent and X_0 that in the raw sewage, then as shown by Tatham, the relation,

$$P = X_0 F \div (F - L W)$$

holds, where W = the total liquid content of the purification apparatus at time T. The constant, L, has been termed the "avidity constant" and expresses the eagerness with which the sewage takes up oxygen, and is therefore a numerical value of the rate at which the sewage is oxidised. Tables have been drawn up giving the value of the constant for various forms of filters and varying conditions, so that supposing a sewage is required to be purified to say 90%, it is only necessary to determine L in the laboratory with the sewage and the filter material to be used, and refer to the table for the time of contact necessary to produce this purification. The tables and the equations used in getting them must be regarded as provisional till they are proved by actual practice, but as the author points out, they give mathematical expression to various factors, one for instance, well known to those conversant with works practice, that the size of a plant increases very greatly per unit increase in the percentage purification as the latter itself increases. The avidity constant is characteristic jointly of the sewage liquor and the method of purification, so that for a standard sewage the constant depends on the sewage. It would therefore seem that the constant may be split into two constants, one characteristic of the sewage and the other of the method of purification.

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[28] *Brit Med J*, 1916, 817, *J*, 1917, 232.

[29] *J*, 1916, 711.

With the recognition of the fundamental fact that sewage purification should consist of a rapid carbon oxidation by the oxygen of the air, followed by nitrification, the increasing use and development of this form of purification under the name of the "Activated sludge process," causes no surprise. This process, which originated only a few years ago, was put on a firm foundation by the preliminary tests of Arden and Lockett, carried out with Manchester sewage, in which it was shown that if raw sewage is aerated till complete nitrification takes place, the effluent removed and more raw sewage mixed with the sludge, the aeration, if continued as in the first case, will produce purification in a much shorter time. The sludge which accumulates from these processes of aeration is termed "activated sludge," and its beneficial influence in reducing the length of time for aeration and so reducing the size of tanks is so apparent, that plants have now been installed for the tentative treatment of the sewages of such towns as Manchester (Withington Sewage Works), Salford, Worcester, Stamford, Lincoln, and Sheffield, not to speak of large American installations at Milwaukee and Houston (Texas), and other places The phenomenal development of the process which so far has been mainly due to the continuing work of Ardern and Lockett, and the more recent papers by Fowler here[30] and those of Bartow and his colleagues in America,[31] must also be attributed to the effective and economical means of aeration which have been devised by Jones and Attwood. Melling has more recently been experimenting in determining the inhibitory effects of certain trade wastes, and in modifying the forms of plant. The application of the method to weak domestic sewage free from manufacturers' effluents has been experimentally tried with results that show that effluents easily within the standards laid down by the Royal Commission can be obtained with an aeration period smaller than the usual, thus lowering the working costs, and the fears which were anticipated that the process may not give satisfactory results during winter months have proved unfounded. In America the process has been applied to the trade waste of the packing houses at Fort Worth, Texas, and at Chicago. The latter scheme involves 50 million gallons a day; the cost is estimated at £9 per million with a revenue of £5 per million from the nominal value of the sludge, giving a nett cost of £4 per million gallons.

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[30] *J. Inst. San. Eng.*, 1916

[31] *J. Ind. and Eng Chem.* 1915, **7**, 318; 1916, **8**, 14; *J.*, 1915, 508, 1916, 555.

The successful application of the process on a large scale[32] is dependent on the most economical and efficient method of keeping activated sludge in intimate contact with the sewage under strictly aërobic conditions, whilst the methods of performing the minor operations also require consideration and individual care. The process may be carried out in a fill-and-draw tank or in a continuous flow system, of which the first, though more effective and safer in that it avoids short circuiting of the sewage and obviates the difficulty of aeration and putrefaction of the sludge, has the disadvantage of requiring a fall for discharge, increased operation and attention, and increase of diffuser difficulties by the constant periodical settlement of sludge. For these reasons, the continuous flow is the most favoured method, although here a separate settlement tank must be provided to make provision for the return of the sludge to the aeration chamber. Rectangular tanks, divided to reduce possibility of short circuit, and fairly deep to economise the aeration, should be used, and porous diffusers in place of perforated pipes. A pulsating air supply so as to regulate the air supply, especially in times of stormy weather, is also necessary.

The difficulty which, up to the present, has not been overcome is a suitable design for a settlement tank and a means of returning the sludge to the aeration chamber. This failure has the twofold effect of limiting the flow which can be treated satisfactorily by reason of the inadequate settlement afforded, and the inability to avoid sludge retention which results in the return to the aeration chamber of sludge in a more or less putrefactive condition, to the great disadvantage of the process.

The outstanding feature of the activated sludge process is the recovery of a considerable portion of the nitrogen content in a form available for agricultural purposes. The dried sludge contains from 5 to 6% of nitrogen, according to the character of the sewage treated, and also appreciable quantities of phosphates. Experiment has shown that the bacterially precipitated sludge is extraordinarily active as a manure, and Bartow and Hatfield have published photographs of the comparative pot cultures in pure sea sand to which had been added the same amount of plant foods, which show that wheat, clover, and flowering plants, such as lilies and chrysanthemums, gave better results with activated sludge than with such nitrogenous fertilisers as dried blood, nitrate of soda, sulphate of ammonia, or gluten meal.[33] The difficulty which prevents full use being made of the sludge is transportation, as so far no really efficient process has been devised for de-watering and drying at a remunerative cost. In certain localities the sludge is piped directly to farms, which of course receive the full bacterial benefit it is able to give, but unfortunately this cannot be carried out everywhere. The numerous patents for methods and plants for supplying this want are indications that the difficulty is well on its way to being solved, so that the advocates of this system hope that, before long the omnipresent nuisance of sludge disposal will be with us no longer.

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[32] E. Ardern, *J.*, 1917, 822.

The general scarcity of materials which the great war has produced, and will continue to produce so long as it lasts, has drawn attention to means of preventing waste and the recovery of substances from what are usually regarded useless waste products Sewage waste, which nominally comes under the latter category, has therefore come in for its proper share of attention, and processes both here and on the continent have been proposed and carried out for the recovery of anything that may be of value in it.

So far the recovery of the fat has been the main objective of these processes, and a paper by the writer,[34] which was read at the last annual meeting of the Sewage Works Managers' Association, gives interesting figures of the processes so far at work, and suggests other means whereby the nitrogen may be converted into ammonia or nitric acid and the calorific value of the organic matter in the sewage utilised for fuel.

The recovery of fat from sewage sludge has been attempted at Elberfeld-Barmen, where, after removal of fat by solvents, the sludge still containing 50% water is mixed with one-third its weight of coal and burnt as fuel Since by this method the whole of the nitrogen contained in the sewage is lost, E. R Besemfelder[35] recommended that the fat-free sludge be dried and then coked in a furnace by means of producer gas. The hot coke would be discharged directly into the water-gas generators and the mixed lighting gas and water-gas from the furnace treated by methods used in gas works for the recovery of ammonia. Based on the actual results of the recovery of fat from the Elberfeld-Barmen installation and nitrogen content and calorific value of the dry sludge, it was estimated that the sewage sludge in Germany, with its 67 million inhabitants, had a value of £6,000,000; of this amount the crude fat represents 50%, the recovered ammonium sulphate 25%, and the fuel value of the gas 25%.

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[33] *J. Inst. Sanit. Eng*, Feb 2, 1916.

[34] *Chem Trade J.*, 1916, **59**, 371; *J*, 1917, 44

[35] *Chem.-Zeit*, 1915, **39**, 813; *J*, 1916, 193.

The above applies mainly to ordinary domestic sewage. For trade wastes, progress is also being made, and judging from the patent literature, the time does not appear to be far distant when the recovery of trade wastes will form a still more important part of our industrial life, and thus simplify the sewage disposal problem. Tanyard waste still seems best treated with "copperas" precipitation, followed by double filtration, but even then the rate of filtration is slow, the primary filters not taking more than 31 gallons per cube yard. The injury to sewage farm crops by unusual wastes has recently had a further example in the recent action in the High Court, in which it was established that a trade effluent containing boric acid had a cumulative poisonous action on sewage farm soil. Cook and Wilson however[36] have arrived at the conclusion that soluble boric acid and borates when used in quantities sufficient to act as a larvicide in manure heaps, do not harm crops, as they are converted into insoluble and innocuous borate compounds.

DISINFECTANTS.

Since Anderson and McClintic published in 1912, in America, their modified test for disinfectants and introduced the "Hygienic Laboratory phenol coefficient," there has been no other test brought forward in place of the original Rideal-Walker carbolic acid coefficient method, and with the exception of the former test being adopted to some extent in the United States, the Rideal-Walker method is now almost invariably employed for the bacteriological control of disinfectants. However, from further experience gained in the working of the test, attention has been drawn to several details during the last few years.

Subsequent to the limits laid down by Rideal and Walker in 1915 for the resistance of the test organisms to the carbolic acid controls the importance of employing a normal strain of *B. typhosus* has been emphasised. A further point is the purity of the carbolic acid used for control; beyond its standardisation by bromine titration, to check the actual strength of the dilutions, it is necessary to ensure that the original phenol is free from cresol contamination, traces of which alter the germicidal value and are not indicated by the bromine titration. Weiss has suggested the determination of the solidifying point, which should not fall below 40° C.

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[36] *J. Agric. Research*, 1917, **10**, 591, J., 1917.

Owing to the war the question of the peptone for preparing the broth for disinfectant testing has been raised. The supply of Witte peptone, formerly almost exclusively used for bacteriological work, from Germany, has been cut off, and stocks held have become more and more depleted. While some are entirely unsuitable for the preparation of culture media it has been found that the same carbolic acid coefficients are not obtained when different makes of peptone are adopted. In order to obtain concordant results with other observers, it appears to be essential to employ Witte peptone broth at any rate for the test cultures, and for economy many authorities use the Witte peptone only for the test culture, the subcultures being taken over into broth made with some other good peptone readily obtainable. While dealing with this question it is also important to note in the bacteriological examination of waters for the presence of typical *B. coli*, that failure to obtain the indol reaction due to some makes of peptone may lead to erroneous conclusions.

The matter has been brought to a stage further by J. H. Wright,[37] who has recently supervised an extensive enquiry into the importance of uniform culture media in the bacteriological examination of disinfectants, at the Lederle Laboratories, New York. As the result of this work he concludes that most of the discrepancies are due to variation in the culture media, and apart from the question of ingredients the hydrogen-ion concentration has important influences on the growth of bacteria in the medium. Adjustment of the alkalinity to a definite reaction by ordinary phenolphthalein titration does not control the hydrogenionisation. Wright is in favour of no attempt being made to adjust the reaction (by titration) of the culture medium during its preparation. The most satisfactory and uniform results were yielded when the P_H value of the culture medium lies between 6 and 7. He states that this condition is readily obtained by using certain proportions of the ingredients and filtering, &c., with no addition of alkali. At the same time he admits the difficulty and time required before such a change can become the standard procedure.

In spite of the requirements of disinfection brought about by war conditions, there has been little recent advance in the testing of disinfectants in the presence of quantities of organic matter, the many tentative suggestions of several years ago have been more or less abandoned, and at the present time there is no one standard method employed. In the Edinburgh Medical School, at the request of the National Insurance Medical Committee, heavily infected tissues were exposed for definite periods to the different antiseptics, reproducing as far as possible conditions likely to be met with in a wound. P. Delbet[38] and A. Lumière[39] have worked with disinfectants in the presence of pus. Delbet found that a 2% solution of phenol gave the best results out of a number of reagents employed, and this was confirmed by Lumière, the latter stating that oxidising agents, as represented by hypochlorite, are rendered inert unless used in large quantities.

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[37] *J. Bact.*, ii, July 4, 1917

For war purposes the English authorities are extensively employing emulsified coal tar disinfectants, which are required to have a Rideal-Walker carbolic acid coefficient falling between 10 and 12. The official name of "Liquor cresoli saponatus fortis" is somewhat misleading. Under the popular name "cresol" these disinfectant fluids are distributed to the various units abroad, apparently undiluted. Consequently the great demand for this class of disinfectant has to some extent curtailed the production of the higher coefficient preparations with values of upwards of 16. The employment of the fluids having the highest coefficient would reduce the bulk for transport and also minimise the great number of metal containers at present required for this purpose. At the same time, taking the cost of the fluids as proportional to their carbolic acid coefficient values, to ensure economy and prevent waste of these more powerful and expensive fluids, some scheme would be necessary by which the fluid should be kept under proper supervision and brought to the necessary working dilution at the place of disembarkation, or better at divisional or brigade headquarters, before being distributed.

Early in the war the bactericidal properties of malachite green were brought to the notice of the surgical staff at Haslar,[40] and brilliant green has also been used[41] as a differential germicide in typhoid-coli diagnosis, whilst later in the year ethylhydrocupreine hydrochloride was advocated for sterilising fæcal *streptococci*.[42]

Emery in 1916 devised a standard method of testing antiseptics for wounds arising out of his studies of the pathology of gas-gangrene, whilst Almroth Wright advocated the irrigation of wound surfaces with therapeutic or physiological salt solutions alone without any specific germicide. Lorrain Smith, Ritchie, and Rettie suggested the addition of borax to bleaching powder to form a neutral antiseptic containing active hypochlorous acid, which resulted in a powder known as "eupad" and a solution known as "eusol" being introduced. Dr. Dakin's use of the same germicide in the form of electrolysed sea water, and later in the more active combination as a chloramine derivative, has already been referred to under water-sterilisation.[43]

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[38] *Comptes rend.*, 1916, **162**, 36; *J.*, 1916, 193.
[39] *Comptes rend.*, 1916, **163**, 309; *J.*, 1916, 1079.
[40] *Lancet*, July 24, 1915.
[41] *R. A. M. S. Journal*, Oct., 1916.
[42] *Lancet*, Dec. 25, 1915.

The favourable results obtained by the use of electrolysed sea water in the Mediterranean on the H.M. hospital ship "Aquitania," led the War Office and the Cunard Steamship Company to instal similar plants on other ships in 1916, and these have continued to give good results during the year.

It appears that the neutralised hypochlorites (eusol), containing buffer salts, can also be used for intravenous injection, and can be tolerated in comparatively large amounts. It has therefore competed with the germicidal dyestuffs as a powerful antiseptic with low toxicity to the tissues, so that at the present time we may place the hypochlorites and their chloramine derivatives as alternatives to the newer dyestuffs, brilliant green, acriflavine (the English trade name of Ehrlich's trypaflavin, diaminomethylacridine chloride), and proflavine (diamino-acridine sulphate), which have come into prominence during the year as baths and washes for the healing of wounds and for the control of the activities of the leucocytes in cases of septic wounds. The two schools do not apparently make controls one against the other; one would like for example to ascertain the relative weights of "acriflavine" and "halozone," which give equivalent germicidal results in Isle of Wight bee disease.

Zinc sulphate has been reintroduced as a nasal spray and generally for disinfection of cerebro-spinal contacts in competition with acriflavine for this purpose, and bismuth salts (with iodoform) in a paraffin paste for bone dressings and as iodide with emetine in cases of amœbic dysentery, thus trying to combine the virtues in the art of healing.

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[43] See also Rettie, J., 1918, 23 r

FINE CHEMICALS, MEDICINAL SUBSTANCES, AND ESSENTIAL OILS.

By Frank Lee Pyman, D.Sc., Ph.D.

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Commercial Syntheses of Lower Aliphatic Compounds.

Chlorides of methane.—The production of intermediate compounds in the chlorination of methane from natural gas is discussed by C. W. Bedford,[1] who records experiments on the reaction under the light of the white flame arc in the presence of ice, by which very fair yields of methylene chloride and chloroform may be obtained. The interaction of chlorine with 4 to 8 volumes of methane at 400°–600° C. is said to give a mixture of methyl chloride and methylene chloride,[2] whilst the manufacture of methyl chloride can also be conducted by diluting the chlorine with one-third of the methane and treating the mixture with the rest of the methane at 300°–500° C.[3] Methyl chloride is also obtained by the action of phosgene on methane.[4]

$$CH_4 + COCl_2 = CH_3Cl + CO + HCl$$

Chloroform and carbon tetrachloride can be obtained by chlorinating methylene chloride, keeping the temperature between suitable limits (350°–400° C.) by the use of a large excess of methylene chloride as a diluent.[5] Carbon tetrachloride also results from heating a mixture of carbon disulphide and sulphur dichloride.[6]

$$CS_2 + 2SCl_2 = CCl_4 + 2S_2$$

Chloroform may be purified by treatment with strong sulphuric acid.[7]

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[1] C. W. Bedford, *J. Ind. Eng. Chem.*, 1916, **8**, 1090; *J.*, 1917, 46.

[2] B. S. Lacy, U.S. Pat. 1190659 (1916); *J.*, 1916, 907.

[3] B. S. Lacy, Eng. Pat. 101708 (1916); *J.*, 1917, 1563.

[4] A. Hochstetter, Ger. Pat. 292089 (1914); *J.*, 1916, 867.

[5] B. S. Lacy, Eng. Pat. 14709 (1915); *J.*, 1916, 653.

[6] C. J. Strosacker, U.S. Pat. 1204608 (1916); *J.*, 1916, 1271.

[7] G. Michaelis, U.S. Pat. 1203032 (1916); *J.*, 1916, 1272.

Applications of acetylene.—This subject was fully reviewed last year, and there is little new material to report upon. Some modifications of the previous methods of hydrating acetylene to yield acetaldehyde have been described,[8] whilst processes for the regeneration of the mercury catalyst,[9] and the preparation of aluminium alkyloxides with higher homologues of ethyl alcohol have been recorded.[10]

Another method of hydrating acetylene consists in the action of a catalyst, such as bog iron ore at 100° C., on a mixture of 1 part of acetylene with 4 parts of steam, when acetaldehyde results; by substituting ammonia or hydrogen sulphide for steam, and employing other suitable catalysts, acetonitrile and thiophene are obtained respectively.[11]

Ethylidene diacetate, an intermediate product in the preparation of acetic anhydride from acetylene, has been found to be an acetylating agent of general application, the reaction taking place as follows[12]:—

$$(CH_3.CO_2)_2CH.CH_3 + R.OH = CH_3.CO_2R + CH_3.CO_2H + CH_3.CHO.$$

Acetic anhydride.—Acetic anhydride may be prepared by distilling a dry intimate mixture of sodium pyrosulphate and sodium acetate.[13] Another patent describes the use of sulphuric anhydride alone or mixed with chlorosulphonic acid, sodium chloride, or sodium sulphate, in the preparation of acetic anhydride. When sulphuric anhydride is added to anhydrous sodium sulphate and the product mixed with sodium acetate, with acetic anhydride as a diluent, acetic anhydride of a high degree of purity and free from chlorine can be distilled off in a vacuum.[14] The conditions under which the formation of chlorinated by-products may be avoided in the interaction between sodium acetate and sulphur chlorides are described in two patents.[15]

Ethylene and its derivatives.—The preparation of ethylene by the reduction of acetylene with chromous salts has been described.[16]

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[8] Farbw. vorm. Meister, Lucius & Brüning, Ger. Pat. 293070 (1914), addition to 292818; *J.*, 1916, 1082. H. Dreyfus, Fr. Pat. 479656 (1914); *J.*, 1916, 1179. H. Hibbert and H. A. Morton, U.S. Pats. 1213486 and 1213487 (1917); *J.*, 1917, 403.

[9] Chem. Fabr. Griesheim-Elektron, U.S. Pats. 1185499 and 1185500 (1916); *J.*, 1916, 754.

[10] Farbw. vorm. Meister, Lucius & Brüning, Ger. Pat. 293613 (1913), addition to 286596; *J.*, 1916, 1083.

[11] Chem. Fabr. Rhenania, B. K. Staer and W. Gibb, Eng. Pat. 109983 (1916); *J.*, 1917, 1194. [12] G. Boiteau, Fr. Pat. 478,435 (1914); *J.*, 1916, 1131.

[13] H. Dreyfus, Fr. Pat. 478951 (1914); *J.*, 1916, 1179.

[14] H. Dreyfus, Eng. Pat. 17920 (1915); *J.*, 1917, 562.

[15] H. Dreyfus, Eng. Pat. 100450 and 100452 (1916); *J.*, 1917, 614, 668.

[16] W. Traube, Ger. Pats. 287565 (1913), and 295976 (1914); *J.*, 1916, 142; 1917, 569.

Newth's method [17] of preparing the gas by the action of phosphoric acid on alcohol has been modified by two workers,[18] one of whom passes alcohol vapour over heated phosphoric acid instead of adding the liquid alcohol to the acid. The oil ("ethylene petrol") which is obtained as a by-product in Newth's process has been found to consist of a mixture of hydrocarbons, including several homologues of *cyclo*-hexane.[19]

Unsaturated hydrocarbons are present to the extent of about 5 % in the so-called heavy oil of wine—mainly consisting of ethyl sulphate—obtained by the action of concentrated sulphuric acid on ethyl alcohol.[20]

A new method for the preparation of ethylene consists in passing alcohol vapour over thin layers of aluminium sulphate upon inert material at 350°–400° C.,[21] and recalls the use of aluminium sulphate[22] as a catalyst in the preparation of the gas by the action of sulphuric acid on ethyl alcohol.

In the preparation of ethylene dibromide, it has been found to be economical to pass ethylene up a tube down which bromine vapour is falling.[23]

Ethylene dichloride can be prepared from ethylene and chlorine in good yield if the temperature of the mixture is kept at 0° C., whereas at higher temperatures large quantities of trichloroethane are formed.[24] The use of calcium chloride as a catalyst in the formation of ethylene dichloride has been recommended.[25]

Ethylene dichloride may be converted into ethylene glycol by heating with ferric oxide,[26] or with an alkali formate and an alcohol under pressure.[24] It is also claimed that polyhydric alcohols are produced by heating chlorinated hydrocarbons with dilute aqueous alkali carbonates in the presence of copper.[27]

Ethylene bromohydrin is readily produced together with about its own weight of ethylene dibromide by the action of bromine water on ethylene at 0° C.[28]

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[17] *Chem. Soc. Trans.*, 1901, **79**, 915; *J.*, 1901, 757.

[18] E. B. R. Prideaux, *Chem. News*, 1916, **113**, 277; *J.*, 1916, 754. J. A. Smythe, *Brit. Assoc.* 1916; *J.*, 1916, 1130.

[19] De Montmollin, *Bull. Soc. Chim.*, 1916, **19**, 242; *J.*, 1916, 906.

[20] R. Kremann, *Monatsh.*, 1917, **38**, 53; *J.*, 1917, 905.

[21] A. Hough, U.S. Pat. 1206222 (1916); *J.*, 1917, 100.

[22] J. B. Senderens, *Compt. rend.*, 1910, **151**, 392; *J.*, 1910, 1081.

[23] Prideaux, *loc. cit.*

[24] B. T. Brooks and I. Humphrey, U.S. Pat. 1215903 (1917); *J. Ind. Eng. Chem.*, 1917, **9**, 750; *J.*, 1917, 472, 1028.

[25] Smythe, *loc. cit.*

[26] Hough, *loc. cit.*

[27] O. Matter, U.S. Pat. 1237076 (1917); *J.*, 1917, 1065.

Ether.—A continuous process for the production of ether from alcohol and sulphuric acid has been described,[29] and the esterification of sulphuric acid by ethyl alcohol has been studied quantitatively.[30] The purification of ether by boiling and stirring it with caustic alkali has been patented,[31] and Pharmacopœial standards and tests for ether for anæsthesia have been discussed.[32]

Synthetic fusel oil.—Synthetic commercial amyl acetate and fusel oil can be prepared by the following operations. A gasoline, boiling at 25°–45° C., and consisting chiefly of saturated hydrocarbons, as for instance that obtained by cooling natural gas, is chlorinated by introducing chlorine at one end of a body of the hydrocarbon whilst illuminating the other end with a source of actinic light, and causing the gas to approach the light. By this means monochloro-derivatives are obtained, and as soon as these have accumulated to the extent of 20%, the mixture is fractionated, and the unchanged hydrocarbons are recovered for re-treatment. The fraction, b.pt. 95°–110° C., consisting mainly of pentyl and hexyl chlorides, is heated with an equal weight of anhydrous sodium acetate (with or without acetic acid and amyl acetate) for 5 hours at 200° C. under pressure in an autoclave rotated 30 times per minute. In this way, 580 lb. of the crude chlorides gave 384 lb. of crude amyl acetate, from which fusel oil may be obtained by hydrolysis.[33] Another method for the production of fusel oil consists in heating the chlorides with methyl alcohol and a formate under pressure at 140°–190° C.[34]

Synthesis of tartaric acid.—A process has been protected for the production of tartaric acid synthetically. Carbon monoxide and an alkali hydroxide combine at 180°–220° C. to give a formate which yields the corresponding oxalate when heated at 360°–410° C. under pressure. This can be reduced by an amalgam in the presence of lead, to a glyoxylate, which yields racemic and mesotartaric acids on electrolytic reduction in alkaline solution.[35]

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[28] J. Read and M. M. Williams, *Chem. Soc. Trans.*, 1917, **111**, 240; *J.*, 1917, 613.

[29] F. Barbe, et Fils et Cie, Fr. Pat. 479133 (1914); *J.*, 1916, 1179. Eng. Pats. 100496 and 101724 (1916); *J.*, 1917, 569, 1064.

[30] P. N. Evans and J. M. Albertson, *J. Amer. Chem. Soc.*, 1917, **39**, 456; *J.*, 1917, 472.

[31] G. Michaelis, U.S. Pat. 1189502 (1916); *J.*, 1916, 907.

[32] E. Mallinckrodt, junr., and A. D. Ait, *J. Ind. Eng. Chem.*, 1916, **8**, 807; *J.*, 1916, 1081. D. B. Dott, *Pharm. J.*, 1917, **98**, 236; *J.*, 1917, 402.

[33] H. Essex, H. Hibbert and B. T. Brooks, *J. Amer. Chem. Soc.*, 1916, **38**, 1368; *J.*, 1916, 906. B. T. Brooks, H. Essex and D. F. Smith, U.S. Pat. 1191916 (1916); *J.*, 1916, 944. H. Essex and B. T. Brooks, U.S. Pat. 1197019 (1916); *J.*, 1916, 1082. H. Hibbert, H. Essex and B. T. Brooks, U.S. Pat. 1214919 (1917); *J.*, 1917, 403.

[34] B. T. Brooks and H. Essex, U.S. Pat. 1221667 (1917); *J.*, 1917, 569.

Effect of the War on Medicinal Substances.

The position of the fine chemical industry in this country has been the subject of several papers,[36] some of which were read before the Society. The variation of price in certain synthetic drugs from July, 1914, to January 1, 1917, was given in the last report, and the subsequent changes are recorded below:—

		January 1, 1917.		January 1, 1918.	
		s.	d.	s.	d.
Acetanilide	per lb.	2	10	1	9
Acetylsalicylic acid	„	18	6	14	0
Hexamine	„	2	9	5	6
Phenacetin	„	92	6	35	0
Phenazone	„	33	0	55	0
Salol	„	10	6	10	0
Salicylic acid	„	4	9	6	0
Sodium salicylate	„	5	9	7	3

The most striking change in price is the drop from 92s. 6d. to 35s. in the case of phenacetin, due to increased production and competition in allied and neutral countries. Generally speaking, however, there is an upward tendency due to the continual rise in the cost of labour and materials. An example of the increased cost of materials is given by the *Chemist and Druggist*[37] in an article dealing with the economic position of salicylates. It was pointed out that before the war, when salicylic acid was selling at about 1s. per lb., phenol cost 3½d. per lb., and caustic soda £3 per ton, whereas at the time of writing (August, 1916) these materials cost 2s. per lb. and £20 per ton respectively. Details of the fluctuation in price of many other synthetic drugs are given in an article by J. C. Umney, which has been abstracted in the Journal.[38] In a lecture delivered before the Royal Society of Arts,

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[35] L. H. Baekeland and A. H. Peel, U.S. Pat. 1190845 (1916); *J.*, 1916, 924.

[36] D. B. Dott, *J.*, 1916, 788; F. H. Carr, *J.*, 1916, 789, 949; C. A. Hill and T. D. Morson, *J.*, 1917, 792; F. W. Mann, *J.*, 1917, 830.

[37] *Chem. and Drugg.*, 1916, 88; *J.*, 1916, 978.

[38] *J.*, 1917, 72.

F. A. Hocking[39] dealt with the drugs used in the London Hospital before the war, and the extent of our dependence upon Central Europe for their supply. Of drugs, in the sense of original materials, about 80 were employed, including flavouring and perfuming agents, only eight of these were derived from enemy countries, namely, aconite root, belladonna root and leaves, colchicum corm, digitalis leaves, gentian root, henbane leaves, opium, and possibly valerian root, and real difficulties of supply were only met with in the case of belladonna root and leaves, henbane leaves, and possibly valerian root. Of 15 substances obtained from the animal kingdom, only one—lanoline—was exclusively German. Fifteen alkaloids were employed and of these seven, namely, apomorphine, acetomorphine, codeine, caffeine, strychnine, quinine, and emetine, were manufactured in England on a large scale, cocain and theobromine were manufactured in this country, but relative not on a large scale, whilst it was stated that we were undoubted dependent on Germany for the remaining alkaloids in the list, whic included atropine, homatropine, and eserine. This statement requir modification, however, for it is within the writer's knowledge that larg quantities of these alkaloids were made in this country prior to the wa Of the 20 acids, four, including lactic and tannic acids, were probabl German. The next group comprised inorganic salts, the majority of which were manufactured in this country. Then there were 20 simple organic compounds, including alcohol, ether, chloroform, iodoform and phenol, all of which were produced in England. Of the complex organic compounds, about 40 in number, more than 30 came from Central Europe; this class included synthetics, such as antipyrine, chloral-hydrate, novocaine, phenacetin, resorcin, saccharin, salicylic acid and its compounds aspirin and salol, and veronal, together with salvarsan and neosalvarsan. The cultivation of medicinal plants in the British Empire was also discussed in a paper read before the Royal Society of Arts by J. C. Shenstone[40], who cited as indispensable drugs the following: belladonna, henbane, foxglove, colchicum, and perhaps valerian and male fern; whilst D. Hooper[41] has pointed out that half the vegetable drugs of the Pharmacopoeia are indigenous to India, whilst most of the remainder can be cultivated there.

During the period under review a further number of German trade-marks have been suspended or avoided, whilst licences to use some German-owned patents have been granted. The trade-marks of chief interest in this section, which have been avoided or suspended since the beginning of the war, are as follows[42]:

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[39] *J.*, 1917, 370.

[40] *Chem. and Drugg.*, 1917, 89, 411.

[41] *Ibid.*, 1916, 88, 727, 786.

Avoided.	*Suspended.*
Aspirin	Adalin[43]
Formamint	Neosalvarsan
Glycin	Novocain
Lysol	Salvarsan
Metol	Trypaflavine[44]
Sanatogen	
Urotropine	

A list of registered trade-marks, by which monopoly is continued to alien enemies for products of which the English Patents have expired, has been published.[45] Applications for licences to use patents protecting the manufacture of adalin,[43] bromural,[46] salicylic aldehyde,[47] salvarsan,[48] neosalvarsan,[48] and trypaflavine,[49] have been granted

SALICYLIC ACID.

The manufacture and purification of salicylic acid form the subject of several patents. For the manufacture of sodium phenoxide, phenol, sodium hydroxide, and 5 % of sodium sulphite are heated to 250°–280° C. in a grinding ball-mill provided with a hollow trunnion for the escape of steam, and then allowed to cool in a vacuum.[50] For the conversion of this into crude sodium salicylate, a rotating autoclave is employed; carbon dioxide is introduced at first cautiously to avoid undue heating, and later, to give a pressure of 100 lb. per sq. in.; the autoclave is then heated to 120°–140° C. until conversion is complete.[51] The crude sodium salicylate in strong aqueous solution is acidified faintly with sulphuric acid, and passed through masses of intermingled zinc and decolorising charcoal, when it yields pure white salicylic acid on further acidification.[52] An improvement in the method of purifying salicylic acid by distillation with steam is described in another patent.[53] This claims the use of a condensing chamber of which a wall, constructed for instance of woollen canvas, permits the passage of steam but retains the crystals of salicylic acid. The electrolytic oxidation of o-cresol to salicylic acid in sodium hydroxide at 240–250° C. under certain conditions is also the subject of a patent.[54]

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[42] *Ibid.*, 1917, **89**, 920.

[43] *Ibid.*, 106, 215, 730.

[44] *Ibid.*, 890.

[45] *Ibid.*, 69.

[46] *Ibid.*, 1916, **88**, 900.

[47] *Ibid.*, 925, 1235.

[48] *Ibid.*, 701; 1917, **89**, 148, 366.

[49] *Ibid.*, 450.

[50] W. Everitt and Co., Ltd., and W. Everitt, Eng. Pat. 105611 (1916); *J.*, 1917, 614.

[51] W. Everitt and Co., Ltd., and W. Everitt, Eng. Pat. 105612 (1916); *J.*, 1917, 614.

ANTISEPTICS

Two classes of antiseptics have come into prominence for the treatment of wounds, namely, derivatives of hypochlorous acid and certain dyes.

Hypochlorites have been used as antiseptics for a long time,[55] but their application has been restricted by the instability and irritating character of their solutions. Improved preparations have now been introduced by J. Lorrain Smith and his collaborators[56] and by H. D. Dakin. The first preparation is a mixture of equal weights of fine-ground bleaching powder and powdered boric acid, and is known as "eupad." Twenty-five grams of this mixture shaken with a litre of water, allowed to stand for a few hours, and filtered, give a solution "eusol" containing free hypochlorous acid 0·51 %, calcium biborate 1·28 %, and calcium chloride 0·17 %. Dakin's solution[57] is a balanced mixture of hypochlorite and polyborates of sodium with small amounts of free hypochlorous and boric acids. For its preparation, 140 grams of anhydrous sodium carbonate are dissolved in 10 litres of tap water, and 200 grams of bleaching powder are added; after thorough shaking, the solution is filtered, and 40 grams of boric acid are added to the filtrate. The solution prepared in this way contains 0·5 to 0·6 % of sodium hypochlorite.

A study of the mode of action of hypochlorites has led to important developments; when hypochlorites act on proteins, amino-groups

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[52] W. Everitt and Co., Ltd., W. Everitt, and C. G. Jackson, Eng. Pat. 105613 (1916); *J.*, 1917, 614.

[53] R. J. Pugh, Eng. Pat. 106516 (1916); *J.*, 1917, 907.

[54] V. Pumilio, Eng. Pat. 103709 (1916); *J.*, 1917, 382.

[55] For a historical note on the subject, see H. D. Dakin, *Brit. Med. J.*, 4 Dec., 1915, 809.

[56] J. Lorrain Smith, A. M. Drennan, T. Rettie, and W. Campbell, *Brit. Med. J.*, 24 July, 1915, 129.

[57] H. D. Dakin, *Comptes rend.*, 1915, **161**, 150; *Brit. Med. J.*, 28 Aug., 1915, 318; *Proc. Roy. Soc.* B., **89**, 232; *J.*, 1915, 919, 977; 1916, 651.

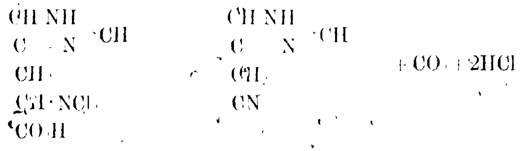
(:NH) in the latter are chlorinated, forming substituted chloro-amines containing the group :NCl, and these also have antiseptic properties.

Dakin has found that the chloroamides of aromatic sulphonic acids are specially suitable for use as antiseptics, and recommends the use in medicine of one member of the class sodio-*p*-toluenesulphonchloroamide, $CH_3·C_6H_4·SO_2·Na·NCl$. The germicidal action of this substance when tested against the ordinary organisms found in infected wounds was equal to that of sodium hypochlorite. In addition it is much less irritating than the latter and may be used safely at a concentration five to ten times as great. This substance, which was first prepared by Chattaway[58] by the action of sodium hydroxide on *p*-toluenesulphondichloroamide, is obtained more economically by the action of alkaline sodium hypochlorite on *p*-toluenesulphonamide; it is also known as "chloramine-T," "chlorazene," and "tolamine."

Sodio-*p*-toluenesulphonchloroamide chlorinates the amino-group of amino-acids forming mono- or dichloro-amines, which break down into aldehydes and cyanides respectively. Thus the monochloro-amine of glycocoll gives formaldehyde:

$$NHCl·CH_2·CO_2H + H_2O = H·CHO + CO_2 + NH_4Cl,$$

whilst the dichloro-amine of histidine gives cyanomethylglyoxaline.[59]



$$\begin{array}{l} CH·NH \\ C—N \end{array} \!\!>\! CH \quad \begin{array}{l} \\ CH_2 \\ CH·NCl_2 \\ CO_2H \end{array} = \begin{array}{l} CH·NH \\ C—N \end{array} \!\!>\! CH \quad \begin{array}{l} \\ CH_2 \\ CN \end{array} + CO_2 + 2HCl$$

The last reaction is of some practical importance, since the product is obtained in good yield and is known to give on reduction the physiologically active base β-iminazolylethylamine (aminoethylglyoxaline).[60]

Closely related to sodium *p*-toluenesulphonchloroamide are *p*-sulphondichloroamidobenzoic acid, $NCl_2·SO_2·C_6H_4·CO_2H$, which has been introduced for the disinfection of drinking water under the name "halazone,"[61] and *p*-toluenesulphondichloroamide, $CH_3·C_6H_4·SO_2·NCl_2$ ("dichloramine-T") which is employed, dissolved in oil, as a nasal antiseptic.[62] For a fuller consideration of recent work on antiseptics, a review by H. D. Dakin[63] may be consulted.

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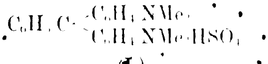
[58] *Chem. Soc. Trans.*, 1905, **87**, 155.

[59] H. D. Dakin, *Brit. Med. J.*, 17 June, 1916, 852; *Biochem. J.*, 1916, **10**, 319.

[60] H. S. Wellcome and F. L. Pyman, Eng. Pat. 28528 (1910); *J.*, 1911, 923.

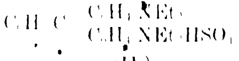
[61] H. D. Dakin and F. K. Dunham, *Brit. Med. J.*, 26 May, 1917, 682.

Certain dyes which were previously known to have trypanocidal properties have been found to be antiseptics of promise.[64] They are distinguished by the fact that they show little deleterious effect on phagocytosis in concentrations which have a strong bactericidal action. Those submitted to investigation were malachite green (I), brilliant-green (II), crystal violet (III), ethyl-violet (IV) and acriflavine (V).



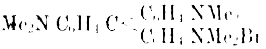
$$C_6H_5\cdot C\Big<\begin{array}{l}C_6H_4\cdot NMe_2\\ C_6H_4:NMe_2\cdot HSO_4\end{array}$$

(I.)



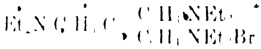
$$C_6H_5\cdot C\Big<\begin{array}{l}C_6H_4\cdot NEt_2\\ C_6H_4:NEt_2\cdot HSO_4\end{array}$$

(II.)



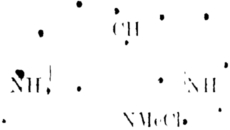
$$Me_2N\cdot C_6H_4\cdot C\Big<\begin{array}{l}C_6H_4\cdot NMe_2\\ C_6H_4:NMe_2Br\end{array}$$

(III.)



$$Et_2N\cdot C_6H_4\cdot C\Big<\begin{array}{l}C_6H_4\cdot NEt_2\\ C_6H_4:NEt_2Br\end{array}$$

(IV.)



(V.)

Of these, brilliant-green and acriflavine were submitted to clinical trial, and proved satisfactory, the latter being both the more efficient and the more rapid in its action. Acriflavine is 3:6-diaminomethylacridinium chloride, which was first prepared by Benda[65] at Ehrlich's request, and used in trypanosomiasis under the name of trypaflavine. When recommended as an antiseptic by Browning and his collaborators[64] it was first given the name flavine, which has since been amended to acriflavine[66] to avoid confusion with an existing vegetable dye bearing the same name. The preparation of acriflavine is the subject of an English Patent,[67] and seven firms applied to the Board of Trade for licences to manufacture it.[68] In view of the interest taken in this compound, it may be well to recall the method of its preparation.

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[62] E. K. Dunham and H. D. Dakin, *Brit. Med. J.*, 30 June, 1917, 865.

[63] *Brit. Med. J.*, 23 June, 1917, 835.

[64] C. H. Browning, R. Gulbransen, E. L. Kennaway and L. H. D. Thornton, *Brit. Med. J.*, 20 Jan., 1917, 73; *J.*, 1917, 161.

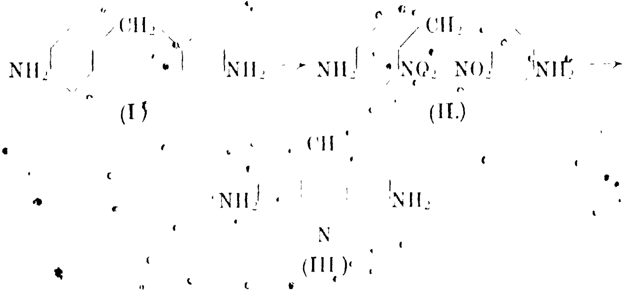
[65] *Ber.*, 1912, **45**, 1787; *J.*, 1912, 678.

[66] *Brit. Med. J.*, 9 June, 1917, 769.

[67] L. Cassella and Co., Eng. Pat. 24652 (1910); *J.*, 1911, 1306.

[68] *Chem. and Drug.*, 1917, **89**, 346, 370, 385, 404, 430, 444, 450, 502, 585, 609, 890.

Aniline and formaldehyde combine to yield 4.4′-diaminodiphenylmethane (I), the 2.2′-dinitro-derivative (II) of which yields 2.2′.4.4′-tetraminodiphenylmethane on reduction with tin and hydrochloric acid. Without isolating the tetramine, the reduction liquor is autoclaved, when 3.6-diaminoacridine (III) results.



In order to avoid methylating the amino-groups of this base, it is first acetylated and then treated with methyl chloride; on heating the product with hydrochloric acid the acetyl groups are removed and acriflavine is obtained. More recently, it has been found that acriflavine can be replaced by the intermediate 3.6-diaminoacridine sulphate, which has been termed 'proflavine'[69]. This substance is an equally effective antiseptic, and is cheaper to produce than acriflavine.

Comparison of the relative bactericidal values of acriflavine and other antiseptics has given varying results in the hands of different authors, and has led to a controversy in the medical press as to the most suitable bacteriological test for antiseptics designed for use in the treatment of war-wounds.

HYPNOTICS.

Attempts to improve upon "veronal" (diethylbarbituric acid) by the introduction of substituents other than the ethyl group into barbituric acid are being continued. A few years ago, phenylethylbarbituric acid was introduced under the name "luminal". Now, it is claimed that barbituric acids containing an alkyl or aryl substituent and an alicyclic or secondary alkyl substituent, such as the isopropyl group (I), have a more powerful hypnotic action than other symmetrical and and unsymmetrical disubstituted barbituric acids[70], whilst barbituric acids containing an alkyl or aralkyl and an aryloxyalkyl substituent—for example, CC-benzylphenoxyethylbarbituric acid (II)—possess strong hypnotic action combined with low toxic effects.[71]

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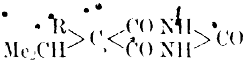
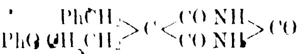
[69] L. Colledge, H. Drummond, R. T. Worthington, J. W. McNee, A. F. Sladden, and J. E. McCartney, *Lancet*, 3 Nov., 1917, 676.

[70] Farbenfabr. vorm. F. Bayer and Co., Ger. Pat. 293163 (1915); J., 1916, 180.



$$\begin{matrix}R \\ Me_2CH\end{matrix}>C<\begin{matrix}CO.NH \\ CO.NH\end{matrix}>CO$$

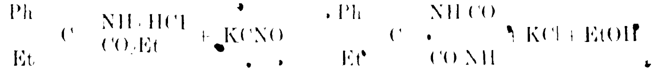
(I.)



$$\begin{matrix}PhCH_2 \\ PhO.CH_2.CH_2\end{matrix}>C<\begin{matrix}CO.NH \\ CO.NH\end{matrix}>CO$$

(II.)

Instead of barbituric acid, which is a six-membered cyclic ureide, hydantoin—a five-membered cyclic ureide—may be employed successfully as the framework of a hypnotic. When phenyl and ethyl substituents are introduced into the hydantoin nucleus, a compound, termed "nirvanol," is obtained, which has a hypnotic action of about the same intensity as phenylethylbarbituric acid, but is distinctly less toxic.[72] This substance is prepared by the action of potassium cyanate on the hydrochloride of ethyl α-amino-α-phenylbutyrate:[73]



$$\begin{matrix}Ph \\ Et\end{matrix}>C<\begin{matrix}NH_2.HCl \\ CO_2Et\end{matrix} + KCNO = \begin{matrix}Ph \\ Et\end{matrix}>C<\begin{matrix}NH.CO \\ CO.NH\end{matrix}> + KCl + EtOH$$

A study of the relative effects of different alkyl groups on the hypnotic properties of dialkylacetyl derivatives of urethane indicated that an increase from two to four in the number of carbon atoms in each group accentuated the narcotic effect. Diethylacetylurethane, "detonal," $Et_2CH.CO.NH.CO_2Et$, and ethylpropylacetylurethane, "epronal," were more effective than urethane, "epronal" being almost equal to "veronal."[74]

Local Anaesthetics

The method of preparation of β-eucaine was recorded in the Report[75] last year. Improvements in the process have now been described by different workers.

A. T. King, F. A. Mason, and S. B. Schryver[76] find that the condensation of diacetoneamine with diethylacetal in the place of paraldehyde gives a much improved yield (90%) of vinyldiacetoneamine; a method for the preparation of this and other acetals, devised by King and Mason,[77] consists in allowing acetaldehyde and the alcohol to react in the presence of a metallic salt, such as calcium chloride, when the acetal is formed in good yield (90%) in the case of diethylacetal.

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[71] Farbenfabr. vorm. F. Bayer and Co., Ger. Pat. 295492 (1915); J., 1917, 306.

[72] E. Wernecke, *Deut. Med. Woch.*, 1916, 42, 1193; J., 1917, 46.

[73] Farbw. vorm. Meister, Lucius und Bruning, Eng. Pat. 105,719 (1916); J., 1917, 615.

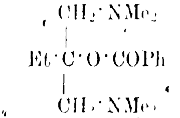
[74] J. Odaira, *Mem. Coll. Sci., Kyoto Imp. Univ.*, 1916, 1, 319; J., 1917, 162.

[75] *Ann. Report*, 1916, 277.

[76] Eng. Pat. 101738 (1916); J., 1916, 1235.

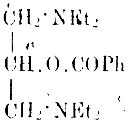
Judd and Kon[78] find that when vinyldiacetoneamine is reduced by means of sodium and amyl alcohol, the hydroxypiperidine is obtained in good yield and in the stable modification, a special operation to isomerise the product being therefore unnecessary.

A certain amount of experimental work on the preparation of local anaesthetics has been recorded, a number of substances constitutionally similar to known examples having been described. Compounds of the eucaine type are obtained by the esterification of 4-hydroxypiperidine and its homologues with aromatic acids,[79] the requisite amino-alcohols being obtained by the reduction of 4-hydroxypyridine (γ-pyridone) and its homologues.[80] Similar to "alypine" (I) is the benzoate of ββ-tetraethyldiaminoisopropyl alcohol (II).[81]



$$\begin{array}{c} CH_2\cdot NMe_2 \\ | \\ Et\cdot C\cdot O\cdot COPh \\ | \\ CH_2\cdot NMe_2 \end{array}$$

(I)



$$\begin{array}{l} CH_2\cdot NEt_2 \\ | \\ CH.O.COPh \\ | \\ CH_2\cdot NEt_2 \end{array}$$

(II)

All the above compounds are stated to have local anaesthetic action and have been protected by patents. It has been found that the replacement of the *p*-aminobenzoyl group in ethyl *p*-aminobenzoate ("anaesthesine") and *β*-diethylaminoethyl *p*-aminobenzoate ("novocaine") by the *p*-aminophenylacetyl group gives substances having no local anaesthetic action.[82] Attempts to prepare soluble and physiologically active derivatives of anaesthesine by condensation with isethionic and lactic acids proved unsuccessful.[83] The next higher homologue of the amino-alcohol of novocaine is employed in the preparation of other local anaesthetics, for which γ-diethylaminopropyl alcohol is esterified with cinnamic, anisic, or *p*-toluic acid.[84] The first of these esters, introduced as "apothesine" has been the subject of a favourable clinical report.[85] The commercial utilisation of anhydroecgonine (II), which is a by-product in the manufacture of cocaine (I), has been the subject of research, and it is found that the ethyl ester of anhydroecgonine yields a saturated alcohol (III) named homotropine, when reduced with sodium and alcohol.

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[77] Eng. Pat. 101428 (1916); *J.*, 1916, 1131.

[78] Eng. Pat. 103541 (1916); *J.*, 1917, 356.

[79] B. Emmert, Ger. Pat. 292846 (1916); *J.*, 1916, 1082.

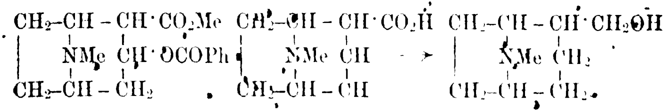
[80] B. Emmert, Ger. Pat. 292456 (1915); 292871 (1915); *J.*, 1916, 868, 944.

[81] L. Thorp, U.S. Pat. 1193634 (1916); *J.*, 1916, 979.

[82] F. L. Pyman, *Chem. Soc. Trans.*, 1917, **111**, 167; *J.*, 1917, 472.

[83] E. Salkowski, *Ber.*, 1916, **49**, 1373; 1917, **50**, 637.

[84] E. A. Wildman and L. Thorp, U.S. Pats. 1193649, 1193650, 1193651 (1916); *J.*, 1916, 979.



(I) (II) (III)

This alcohol has no pronounced physiological action, but when esterified with benzoic, mandelic, or tropic acid yields compounds which have an atropine-like action. The tropyl ester is specifically mentioned as a powerful mydriatic[86]. In a recent lecture on the relation between chemical constitution and physiological action the connection between the structure of an aminoalkyl ester and its local anæsthetic action is discussed[87].

ALKALOIDS.

The mode of formation of alkaloids in plants has been the subject of much speculation. Many of the earlier hypotheses postulated reactions for which there was no analogy in laboratory practice. An important paper and one full of interest by R. Robinson[88] has appeared which is free from this objection. It deals with possible phytochemical syntheses of many alkaloids, including atropine, cocaine, coniine, pelletierine, sparteine, quinine, and the alkaloids of the isoquinoline group, including morphine. Syntheses of these alkaloids from the amino-acids ornithine and lysine, and the degradation products of citric acid and carbohydrates are described in some detail. The difficulty of building up carbon-to-carbon linkages is surmounted in a simple manner by the aid of two processes only, namely, the aldol-condensation and the similar condensation of carbinol-amines with substances containing a reactive methylene group. Both these condensations can be carried out in the laboratory without involving the use of high temperatures or vigorous reactions. The aldol-condensation has been successfully applied by the same author[89] to the synthesis of tropanone from succindialdehyde, acetone, and methylamine,

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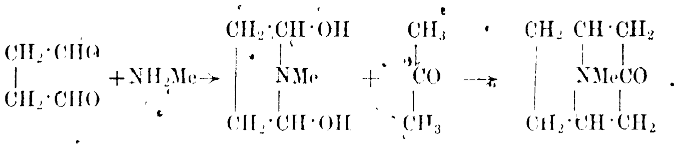
[85] C. W. Allen, *Amer. J. Surg.*, April, 1917.

[86] Chem. Werke Grenzach Akt.-Ges., Ger. Pats. 296742, 299806 (1916); *Centralblatt*, 1917, i, 612; ii, 510.

[87] F. L. Pyman, *Chem. Soc. Trans.*, 1917, **111**, 1103; *J.*, 1918, 72 A.

[88] *Chem. Soc. Trans.*, 1917, **111**, 876; *J.*, 1917, 1147.



$$\begin{array}{l} CH_2\cdot CHO \\ | \\ CH_2\cdot CHO \end{array} + NH_2Me \rightarrow \begin{array}{l|l} CH_2 & CH\cdot OH \\ & | \\ & NMe \\ & | \\ CH_2 & CH\cdot OH \end{array} + \begin{array}{c} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{array} \longrightarrow \begin{array}{l|ll} CH_2 & CH & CH_2 \\ & | & | \\ & NMe & CO \\ & | & | \\ CH_2 & CH & CH_2 \end{array}$$

whilst the condensation of carbinol-amines of the cotarnine type with derivatives of meconine led earlier to the synthesis of narcotine.[90]

K. Hess and A. Eichel[91] have discussed the phytochemical origin of the alkaloids of the pyrrolidine and piperidine groups. They, also, presume that the starting materials are ornithine, lysine, and a degradation product of a sugar, but do not elaborate the mechanism of the syntheses.

Demethylation -To the methods for the demethylation of alkaloids, described in the last report,[92] there may be added a third; it is found that codeine-oxide yields norcodeine and formaldehyde when heated with dilute chromic acid[93] The physiological investigation of the homologues of normorphine, referred to last year has given disappointing results. With the exception of the N-allyl derivatives, all the numerous O-ethers of normorphine and N-alkyl-derivatives of norcodeine which were examined had properties similar to, but much weaker than, those of codeine. The action of the N-allyl derivatives was quite different, being antagonistic to that of morphine.[94]

Methylation -The use of formaldehyde in methylating alkaloids has been the subject of several papers and patents.[95] Aminoalcohols yield N-methylaminoketones when heated with formaldehyde and hydrochloric acid, the N-methylolamino-alcohol first produced suffering simultaneous reduction of the methylol group and oxidation of the alcoholic to a ketonic group.

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[89] *Ibid*, 762, *J*, 1917, 1062.

[90] W. H. Perkin, jun and R. Robinson, *ibid*, 1911, **99**, 775; *J*, 1911, 646.

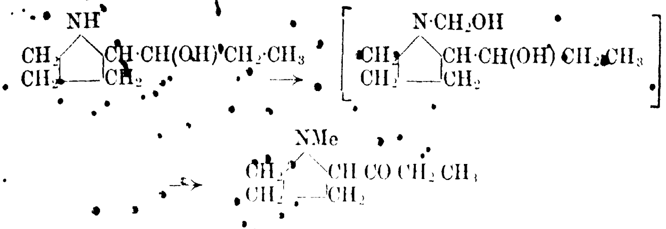
[91] *Ber.*, 1917, **50**, 1407

[92] *Ann Report*, 1916, 287.

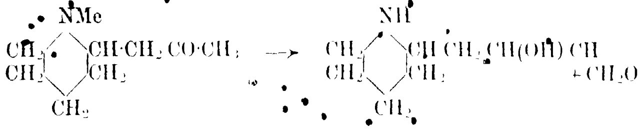
[93] O Diels and Ernst Fischer, *Ber*, 1916, **49**, 1721; *J.*, 1916, 1032.

[94] J. v. Braun, *ibid*, 977; *J*, 1916, 753.

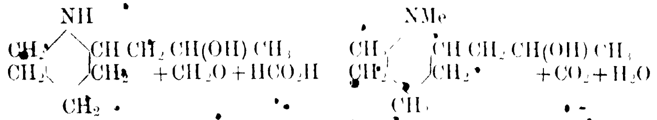
[95] K. Hess and collaborators, *Ber*, 1913, **46**, 4104; 1915, **48**, 1886, 1974; 1917, **50**, 344, 351, 1407; U S Pat 1158496 (1915); *J.*, 1916, 275; Farbenfabr. vorm. F. Bayer and Co, Ger Pats 287802 (1913); 291222 (1914). Addition to 287802; 297847 (1915); *J.*, 1916, 198, 654.



The reverse of this change can be brought about in the case of α-1-methyl-2-piperidylpropan-β-one by the action of semicarbazide, when α-2-piperidylpropan-β-ol and formaldehydesemicarbazone result.



By a modification of the process consisting of the addition of formic acid or some other easily oxidisable substance, amino-alcohols may be methylated to N-methylamino-alcohols, the reduction of the methylol group taking place at the expense of the formic acid rather than of the alcoholic group of the amino-alcohol.



Colchicine.—E. Merck[96] has described compounds of colchicine containing water ($B_2,3H_2O$) and chloroform ($B_2,CHCl_3$ and $B,CHCl_3$) of crystallisation. The substance free from solvent of crystallisation is described as an almost white amorphous compound, which melts at 142°–147° C. H. W. B. Clewer, S. J. Green, and F. Tutin,[97] however, have shown that the base crystallises free from solvent from ethyl acetate in very pale yellow needles, melting at 155°–157° C.; these authors found the alkaloid in the tubers of *Gloriosa superba*, Linn.

Cryptopine.—The constitution of this alkaloid, which occurs in opium in minute quantities, has been thoroughly investigated by W. H. Perkin, jun.,[98] and proved to be of an unusual type (I). Protopine, which accompanies cryptopine in opium and is found in a large number of plants, is similarly constituted, having the formula II.

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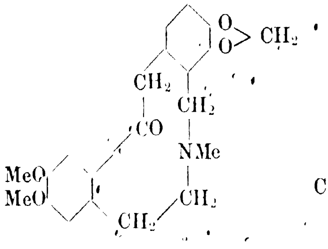
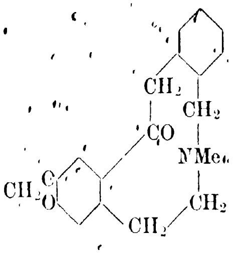
[96] *Chem. and Drug.*, 1916, **88**, 846; from *Apoth.-Zeit.*; *J.*, 1916, 977.

[97] *Chem. Soc. Trans.*, 1915, **107**, 839; *J.*, 1915, 815.

[98] *Chem. Soc. Trans.*, 1916, **109**, 819; *J.*, 1916, 1177.



(I)



(II)

Emetine.—The alkaloids of ipecacuanha and their derivatives have been the subjects of many papers during the period under review. The formula for emetine, $C_{29}H_{40}O_4N_2$, first put forward by Carr and Pyman has since been supported by the analysis of further derivatives by the writer,[99] and has been confirmed by P. Karrer.[100] Keller,[101] however, holds that the evidence is not yet sufficient to distinguish between this formula and $C_{30}H_{44}O_4N_2$. The fact that cephaeline yields emetine on methylation with dimethyl sulphate or sodium methyl sulphate was recorded in 1913,[102] and it has now been found that the methylation can be effected conveniently by the use of nascent diazomethane.[103] Other ethers of cephaeline can be made by alkylating cephaeline with derivatives of alcohols other than methyl alcohol, and the ethyl, propyl, benzyl, allyl,[104] butyl, *iso*butyl, amyl, and *iso*amyl ethers[105] have been described. No important advance has been made in the determination of the constitution of emetine. It has been shown[106] that ipecacuanha contains, besides emetine, cephaeline, and psychotrine, two new alkaloids, one of which is the O-methylether of psychotrine, whilst the relation of the second, emetamine, to the other alkaloids of ipecacuanha is not yet clear. These alkaloids were present in small quantities in all the commercial varieties of ipecacuanha examined, 0·015 to 0·033 % of methylpsychotrine and 0·002 to 0·006 % of emetamine being found.

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[99] *Chem Soc Trans.*, 1917, **111**, 419; *J.*, 1917, 1192

[100] *Ber.*, 1916, **49**, 2057, 1917, **50**, 582; *J.*, 1916, 1177, 1917, 666.

[101] *Arch. Pharm.*, 1917, **255**, 75

[102] H. S Wellcome, F H. Carr, and F. L. Pyman, Eng Pats. 14677 and 17483 (1913), *J.*, 1914, 102, 219

[103] Karrer, *loc. cit.*, Farbw. vorm. Meister, Lucius und Bruning, Ger. Pat. 298678 (1916).

[104] Karrer, *loc cit.*; Farbw. vorm. Meister, Lucius and Bruning, Ger Pat. 301498 (1915); J. W. Meader, Eng. Pats. 11718, 11719 (1915); U S. Pat. 1209575 (1917); *J.*, 1916, 978, 1271; 1917, 520.

[105] J. W. Meader, Eng. Pats. 104642 (1916); 11717 (1915); 105722 (1916); 103881 (1916); *J.*, 1917, 520; 1916, 1271; 1917, 618, 402.

[106] F. L. Pyman, *loc. cit.*

The pharmacology of emetine has been studied by several authors, and many derivatives have been investigated in the hope that they might prove to be more serviceable than the parent alkaloid. Attempts have been made to obtain a preliminary idea of their relative values by comparing their action on amoebae *in vitro*,[107] and two compounds, N-methylemetine and O-methylpsychotrine, proved to be at least equal to emetine in amoebacidal properties and less toxic to animals. On clinical trial, however, they proved to have no advantages over emetine in the treatment of amoebic dysentery.[108] The homologues of emetine, the O-alkylcephaelines referred to above, decrease in toxicity with increase in the size of the alkyl group, the ethyl ether having two-thirds, the propyl ether one-third, and the *iso*amyl ether one fifth of the toxicity of emetine[109], when given subcutaneously, up to the present no information as to their relative therapeutic value has been published.

The favourable clinical results obtained with emetine bismuthous iodide have led to the trial of other insoluble derivatives of emetine, such as "Alcresta" ipecacuanha,[110] an absorption compound of the alkaloids on Lloyd's reagent, and emetine phosphotungstate.[111]

Pelletierine and the accompanying alkaloids. Recent work has revealed the structure of several of the alkaloids of pomegranate bark, which prove to be closely related chemically to the alkaloids of hemlock. The alkaloids previously isolated from the bark were pseudopelletierine, $C_9H_{15}ON$, of which the constitution is known, and the two pairs of isomerides, pelletierine and *iso*pelletierine, $C_8H_{15}ON$, methylpelletierine and *iso*methylpelletierine, $C_9H_{17}ON$. The first mentioned of each of these pairs was optically active, the second optically inactive. K. Hess and A. Eichel,[112] however, have failed to isolate any optically active alkaloids from the material at their disposal, and presume that pelletierine and methylpelletierine of previous workers were optically active forms of *iso*pelletierine and *iso*methylpelletierine respectively. They use the terms pelletierine and methyl*iso*pelletierine for the optically inactive alkaloids previously known as *iso*pelletierine and *iso*methylpelletierine respectively; their nomenclature is adopted below. Pelletierine proved to be an aldehyde which gave β-2′-piperidylpropionic acid (I) on oxidation, and therefore had the formula II. On reduction it gave *dl*-coniine (III).

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[107] F L. Pyman and C M. Wenyon, *J Pharmacol*, 1917, **10**, 237. H. H. Dale and C. Dobell, *J Pharmacol*, 1917, **10**, 399

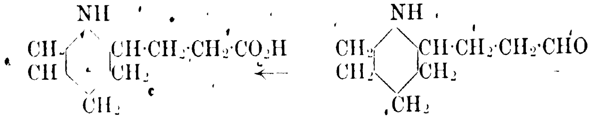
[108] G. C. Low, *Brit Med J*, 13 Nov, 1915, 715; C. M Wenyon and F W. O'Connor, *J. Roy Army Med Corps*, 1917, **28**, 473; M. W Jepps and J C. Meakins, *Brit Med J*, 17 Nov, 1917, 628

[109] Karrer, *loc cit.*, A. L. Walters and E W. Koch, *J. Pharm. Exp. Ther*, 1917, **10**, 73; *J.*, 1917, 1192.

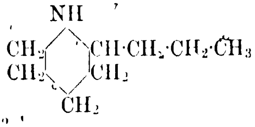
[110] Stephens, *Lancet*, 12 Aug, 1916, 302

[111] G. Nielsen, *Amer J. Clin. Med.*, 1916, **23**, 903, from *Prescriber*, Feb 1917, 50.

[112] K. Hess, *Ber.*, 1917, **50**, 368; K. Hess and A. Eichel, *ibid.*, 380, 1192, 1386.

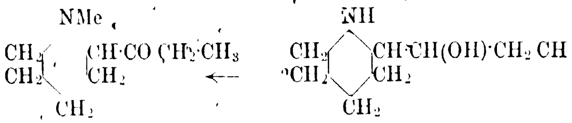


(I) (II)

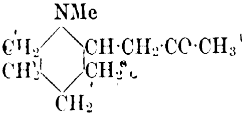


(III)

Its N-methyl-derivative was not identical with methyl*iso*pelletierine, which proved to be 1-methyl-2-piperidyl ethyl ketone (IV), and could be prepared from conhydrine (V) by methylation and oxidation.



(IV) (V)



(VI)

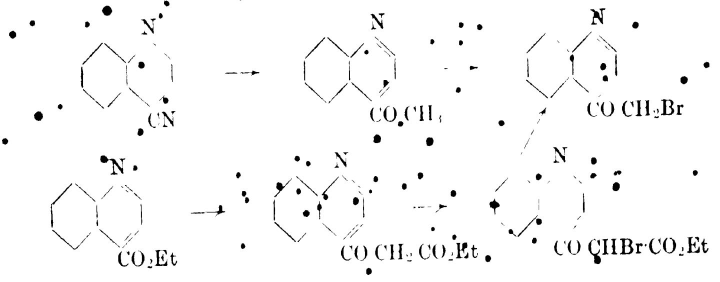
A new alkaloid which was isolated from the bark in the course of the investigation proved to be α-1-methyl-2-piperidylpropan-β-one (VI).

Quinine.—Attention has been drawn to the facility with which quinine bisulphate is transformed to the toxic base quinicine (quinatoxine) on heating. It was recognised previously that this change takes place readily at temperatures above 100° C., but it is now found[113] that the temperature at which quinine bisulphate, heated alone or in very strong solution for 24 hours, first shows decomposition is 60 C., whilst at 90°C. 50 % was decomposed in 24 hours, and 75 in 18 hours.

Substances which resemble the alkaloids of cinchona bark in constitution and physiological action can now be made synthetically. For these syntheses, quinolyl- (or 6-methoxyquinolyl-) ω-bromomethyl ketone is prepared by one of the two methods given below:—

(1) 4-Cyanoquinoline treated with methyl magnesium iodide yields quinolyl methyl ketone, which gives the required compound on bromination.[114]

(2) Ethyl cinchoninate when condensed with ethyl acetate in the presence of sodium ethoxide yields ethyl quinoloylacetate, the bromo-derivative of which gives the bromo-ketone on hydrolysis.[115]



On condensing quinoyl ω-bromomethyl ketone with primary and secondary amines, aminoketones are obtained of the general formula $C_9H_6N.CO.CH_2.NRR_1$, which yield amino-alcohols of the general formula $C_9H_6N.CH(OH).CH_2.NRR_1$ on reduction.[116] The close structural resemblance to quinine of substances synthesised by these methods is shown by the formulæ given below—

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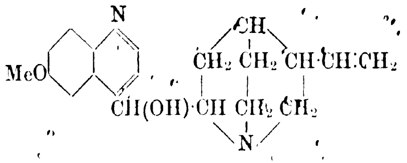
[113] B F Howard and O. Chick, *Chem and Drugg*, 1917, 89, 612, *J*, 1917, 910.

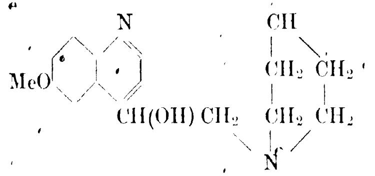
[114] A. Kaufmann, H Peyer and M. Kunkler, *Ber.*, 1912, 45, 3090; A. Kaufmann, Eng Pat 9315 (1913); *J*, 1913, 1130.

[115] P. Rabe and R Pasternack, *Ber*, 1913, 46, 1032; Verein. Chininfabr. Zimmer and Co, Ger. Pat 268830 (1913); *J.*, 1914, 277.

[116] A Kaufmann, *Ber*, 1913, 46, 1823; Ger Pat. 268931 (1913); *J.*, 1914, 277; P. Rabe, R. Pasternack and K. Kindler, *Ber.*, 1917, 50, 144



Quinine



α-6-Methoxyquinolyl-β-piperidinoethyl alcohol.

It is interesting to note that the whole series of aminoalcohols, prepared in this way, were highly toxic to infusoria, paramœcia, etc., but only slightly so to man.

GLUCOSIDES.

Little work on the naturally-occurring glucosides has been published during the period under review, but several papers on the preparation of synthetic glucosides have appeared. The fact that the natural glucosides are usually more active physiologically than their hydrolytic products had led to enquiry as to whether, conversely, glucosides of enhanced physiological activity can be prepared from medicinal substances. The starting material for such syntheses is acetobromoglucose, for which an improved method of preparation has been described.[117] The general method employed has been the condensation of this substance with a compound containing a reactive hydrogen atom, for example an alcohol, phenol, carboxylic acid, or imine, in the presence of alkali, and subsequent removal of the acetyl-groups from the condensation product by hydrolysis. In this way morphine-glucoside,[118] dihydrocupreine-glucoside,[119] and cephaeline-glucoside[120] have been prepared, but they do not appear to have any advantages

[117] E. Fischer, *Ber.*, 1916, **49**, 584.

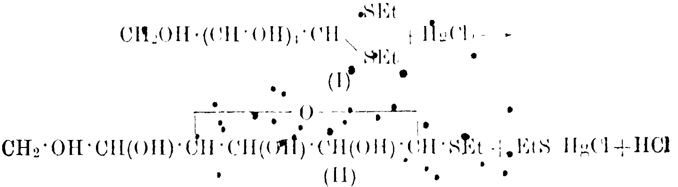
[118] C. Mannich, *Annalen*, 1912, **394**, 223; *J.*, 1912, 1199.

[119] P. Karrer, *Ber.*, 1916, **49**, 1644.

[120] P. Karrer, *Ber.*, 1916, **49**, 2057; *J.*, 1916, 1177.

over the parent compounds. Purine-glucosides,[121] such as theophylline-glucoside, are obtained similarly; they are claimed to be more soluble, less poisonous, and more palatable than the parent substances, but it does not appear that their physiological activity is enhanced. Condensation products of acetobromoglucose with 2-phenylquinoline-4-carboxylic acid (atophan) and salicylic acid have also been obtained, but so far it has not been possible to remove the acetyl groups from the resulting acetylglucosides without effecting further cleavage.[122]

By modifying the method so that the condensation is effected by means of quinoline in the place of alkali, it has been possible to isolate both the α- and β-forms of phenyl- and menthyl-glucosides, and to prepare resorcinyl-β-glucoside in a greatly improved yield.[123] Moreover, the syntheses of *d*- and *l*-mandelonitrile-glucosides, which are identical with sambunigrin and a hydrolytic product of amygdalin respectively, have been effected by a suitable adaptation of the method.[124] In many natural glucosides, the glucose-residue is attached to the remainder of the molecule through a sulphur atom, for instance in the case of sinigrin, the glucoside of mustard seeds. This lends interest to recent work on the synthesis of glucosides of this type. Ethylthioglucoside (II) may be prepared from glucose-ethylmercaptal (I), the condensation product of glucose and mercaptan, by treatment with one molecule of mercuric chloride.[145]



$$\mathrm{CH_2OH\cdot(CH\cdot OH)_4\cdot CH}\begin{matrix}\diagup\mathrm{SEt}\\ \diagdown\mathrm{SEt}\end{matrix} + \mathrm{HgCl_2} \rightarrow$$

(I)

$$\mathrm{CH_2\cdot OH\cdot CH(OH)\cdot}\overbrace{\mathrm{CH\cdot CH(OH)\cdot CH(OH)\cdot CH}}^{\mathrm{O}}\mathrm{\cdot SEt} + \mathrm{EtS\cdot HgCl} + \mathrm{HCl}$$

(II)

Another interesting preparation is that of a disaccharide in which the sulphur atom links together two glucose-residues. This substance, termed thio*iso*trehalose, is formed by the action of acetobromoglucose on potassium sulphide, and subsequent removal of the acetyl groups. Seleno*iso*trehalose can be prepared in a similar manner.[126]

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[121] E. Fischer and B. Helferich, *Ber.*, 1914, **47**, 210; *J.*, 1914, 217. Farbenfabr. vorm. F. Bayer and Co., Ger. Pat. 281008 (1913); *J.*, 1915, 636.

[122] P. Karrer, *Ber.*, 1917, **50**, 833.

[123] E. Fischer and L. von Mechel, *ibid.*, 1916, **49**, 2813; *J.*, 1917, 303; E. Fischer and M. Bergmann, *ibid.*, 1917, **50**, 711.

[124] E. Fischer and M. Bergmann, *ibid.*, 1004; *J.*, 1917, 1288.

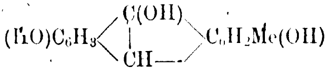
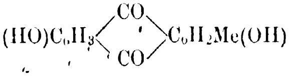
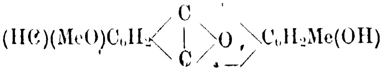
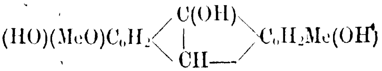
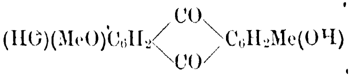
[125] W. Schneider and J. Sepp, *ibid.*, 1916, **49**, 2054.

[126] W. Schneider and F. Wrede, *ibid.*, 1917, **50**, 793.

CHRYSAROBIN.

Commercial chrysarobin, which is used in the treatment of various skin diseases, is a mixture of derivatives of anthracene in varying proportions. The separation of the constituents is difficult, and the processes employed are liable to effect changes in the substances. It is therefore not surprising that different investigators give different accounts of its composition.

F. Tutin and H. W. B. Clewer[127] isolated from three samples of commercial chrysarobin,

chrysophanolanthranol	 $(HO)C_6H_3\left\langle\begin{matrix}C(OH)\\ \vert\\ CH—\end{matrix}\right\rangle C_6H_2Me(OH)$	26—60%
chrysophanol (chrysophanic acid)	 $(HO)C_6H_3\left\langle\begin{matrix}CO\\ \\ CO\end{matrix}\right\rangle C_6H_2Me(OH)$	about 5%
dehydroemodinanthranol monomethyl ether ...	 $(HO)(MeO)C_6H_2\left\langle\begin{matrix}C\\ \vert\\ C\end{matrix}\right\rangle O \rangle C_6H_2Me(OH)$	13–41%
emodinanthranol monomethyl ether	 $(HO)(MeO)C_6H_2\left\langle\begin{matrix}C(OH)\\ \vert\\ CH—\end{matrix}\right\rangle C_6H_2Me(OH)$	small amount
and emodin monomethyl ether ...	 $(HO)(MeO)C_6H_2\left\langle\begin{matrix}CO\\ \\ CO\end{matrix}\right\rangle C_6H_2Me(OH)$	about 2%

In some samples ararobinol and emodin were also found.

Dehydroemodinanthranol monomethyl ether, which formed so large a proportion of the material, was a new compound to which the formula given above was attributed. On heating with hydriodic acid it gave emodinanthranol, whilst chromic acid oxidised it to emodin monomethyl ether. The substance has since been isolated from commercial chrysarobin by R. Eder[128] employing two different methods. By one, commercial chrysarobin was oxidised by air in alkaline solution, and gave 18 % of this constituent, together with chrysophanol (22 %) and emodin monomethylether (10 %), the latter two having been formed from the corresponding anthranols by oxidation; 0·2 % of emodin was also found to be present.

By the second method, commercial chrysarobin was acetylated or benzoylated to prevent oxidation of its constituents during the separation, and was thus found to contain chrysophanolanthranol, emodin monomethyl ether, dehydroemodinanthranol monomethyl ether, and emodin (or emodinanthranol). By this method Eder was unable to detect chrysophanol, chrysarobol, or ararobinol.

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[127] *Chem. Soc. Trans.*, 1912, 101, 290; *J.*, 1912, 253.

[128] *Arch. Pharm.* 1915 **253** 1; 1916, **254**, 1; *J.*, 1915, 681 1917, 1027.

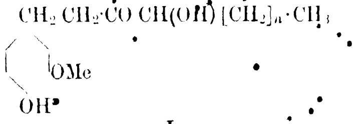
O. Hesse[129] was unable to isolate dehydroemodinanthranol monomethylether from commercial chrysarobin probably owing to his use of an unsuitable method by which it was changed to emodinanthranol, but found the following constituents in three samples:

Chrysophanolanthranol	29–33%
Chrysophanol	1–8%
Emodin	0–1
Emodin monomethylether	0–3%
Emodin anthranol	19–25%
Emodinanthranol monomethyl ether	20–29%
Chrysarobol	3–17%

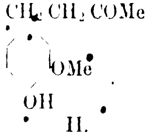
A synthetic product, 1.8-dihydroxyanthranol, is stated to have a much more energetic action upon the skin than its lower homologue, chrysophanolanthranol, and has been introduced into medicine under the name "cignolin."[130]

THE PUNGENT PRINCIPLES OF GINGER.

It has been found[131] that the pungent principle of ginger—"gingerol"—(I)—is a condensation product of *n*-heptaldehyde and lower aliphatic aldehydes with 4-hydroxy-3-methoxyphenylethyl methyl ketone, which is called "gingerone" (II).


$CH_2 \cdot CH_2 \cdot CO \cdot CH(OH) \cdot [CH_2]_n \cdot CH_3$
OMe
OH

I.



II.

The latter substance, which also has pungent properties, has been prepared synthetically by two methods[132] which are described in the contemporary Annual Report of the Chemical Society. It may be noted that "gingerol" has also been isolated—in the form of its methyl ether—from grains of paradise.[133]

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[129] *Annalen*, 1917, **413**, 350; *J.*, 1917, 234.

[130] P. G. Unna, *Dermatol. Wochenschr.*, 1916, No 6-8; *J.*, 1917, 565.

[131] A. Lapworth, (Mrs.) L. K. Pearson, and F. A. Royle, *Chem. Soc. Trans* 1917, **111**, 777; *J.*, 1917, 1062.

[132] H. Nomura, *ibid.*, 769; *J.*, 1917, 1062; A. Lapworth and F. H. Wykes *ibid.*, 790; *J.*, 1917, 1063.

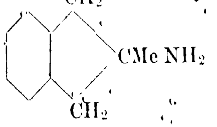
ANIMAL PRODUCTS AND ALLIED COMPOUNDS.

Pituitary gland.—All the therapeutically-used extracts of the posterior lobe of the hypophysis cerebri are found to contain secondary albumoses and possibly polypeptides, which account fully for the biuret and the Pauly reactions, and for the lævo-rotatory power of these extracts. "Hypophysin" is not a solution of the isolated active substances of the pituitary gland, but a mixture of albumoses and possibly polypeptides with varying and unknown amounts of active and inactive constituents of the gland.[134]

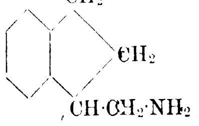
Thyroid gland. Some further particulars of the isolation, chemical properties, and physiological action of the active constituent of the thyroid gland are given. This substance, which was thought previously[135] to be a di-iododihydroxyindole, is now found to contain 65 % of iodine and to have a probable molecular weight 586; it causes hyperthyroidism when given in excessive doses.[136]

Suprarenal gland. The discovery of the constitution of adrenaline, and later, Barger and Dale's work on the relation between chemical constitution and physiological action of the phenylalkylamines, has led to the preparation of alkylamines substituted by nuclei other than benzene. Their work and also that on the glyoxalinealkylamines has been reviewed recently,[137] whilst new work on aromatic alkylamines has been carried out with derivatives of hydrindene and naphthalene.

2-Amino-2-methylhydrindene (I) was found to have a greater effect in raising the blood-pressure than *p*-hydroxy-*β*-phenylethylamine, and its isomerides II, III, and IV were prepared for comparison.



(I)



(II)

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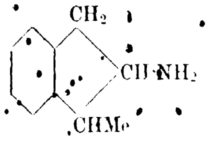
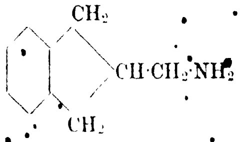
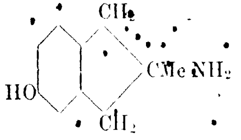
[133] E. K. Nelson, *J. Amer. Chem. Soc.*, 1917, **39**, 1466; *J.*, 1917, 1063.
[134] J. J. Abel and M. C. Rouiller, *Proc. Nat. Acad. Sci.*, 1917, **3**, 507.
[135] E. C. Kendall, *J. Amer. Med. Assoc.*, 1915, **64**, 2042.
[136] E. C. Kendall, *J. Biol. Chem.*, 1917, **29**, 29.
[137] F. L. Pyman, *Chem. Soc. Trans.*, 1917, **111**, 1103.



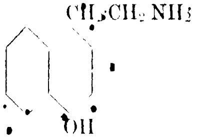
(III)



(IV)



(V)



(VI)

These proved to have a similar action in a quantitative sense, but II was much weaker than I. The introduction of a phenolic hydroxyl group into I, giving the substance V, was not accompanied by an increase in physiological action.[138]

4-Hydroxy-1-β-aminoethylnaphthalene (VI), prepared for comparison with *p*-hydroxy-β-phenylethylamine, proved to be only slightly active.[139]

Vitamines.—The fact that nicotinic acid (pyridine-2-carboxylic acid) is frequently encountered in the search for vitamines has led R. R. Williams[140] to investigate the antineuritic properties of many derivatives of pyridine. Most of them proved to be inactive but the variety of α-hydroxypyridine which crystallises in needles had a curative action. The same author and A. Seidell[141] claim also that adenine acquires antineuritic properties when heated with sodium ethoxide. A. Harden and S. S. Zilva,[142] however, have been unable to confirm the curative properties of either α-hydroxypyridine or adenine, treated as described by these authors.

ESSENTIAL OILS.

A useful review of the manufacturing operations employed in the production of natural and synthetic perfumes has been given,[143] and a description of the lesser known constituents of essential oils, such as myrcene, cuminol, and methyl nonyl ketone, has been published.[144] The relation between odour and chemical constitution has been discussed generally by H. J. Prins,[145] and as applied to aldehydes by L. G. Radcliffe.[146] The last paper deals with aliphatic aldehydes, which are also the subject of another article,[147] whilst an account of aromatic aldehydes and ketones employed in perfumery has also appeared.[148] The odours of benzyl phenylethyl, phenylpropyl, and cinnamyl alcohols, geraniol and citronellol, together with those of their formates, acetates, propionates, butyrates, and valerates have been described and compared,[149] whilst the processes of the manufacture of ionone from citral have been investigated.[150] The recent syntheses of fenchone, fenchene, and santene are briefly described in the contemporary Annual Report of the Chemical Society for 1917. Little new information on the use of essential oils and allied products in medicine is forthcoming, but it may be noted that methylheptenone appears to be a better preventative of lice than anisol,[151] an aqueous solution of thymol is an efficient dentifrice,[152] whilst essence of cinnamon is a valuable prophylactic in measles and German measles.[153] The standards for essential oils in the new United States Pharmacopœia have been critically examined.[154]

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[138] J. v. Braun, O. Kruber and E. Danziger, *Ber.*, 1916, **49**, 2642; J. v. Braun and Z. Koehler, *ibid.*, 1917, **50**, 56; J. v. Braun and E. Danziger, *ibid.*, 286; *J.*, 1917, 234.

[139] A. Windaus and D. Bernthsen-Buchner, *ibid.*, 1120.

[140] *J. Biol. Chem.*, 1916, **25**, 437; *J.*, 1916, 942.

[141] *Ibid.*, 1916, **26**, 431; *J.*, 1916, 1130.

[142] *Biochem. J.*, 1917, **11**, 172; *J.*, 1917, i, 603.

[143] *Perf. and Essent. Oil Rec.*, 1917, **8**, 116.

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[144] *Perf. and Essent. Oil Rec.*, 1917, **8**, 72

[145] *Ibid.*, 222; *J.*, 1917, 912

[146] *Ibid.*, 65

[147] *Ibid.*, 68

[148] L. G. Radcliffe, *ibid.*, 246, 272, 293

[149] H. J. Prins and S. Schwarz, *ibid.*, 1916, **7**, 334

[150] H. F. Slack, *ibid.*, 389; *J.*, 1917, 100

[151] *Ibid.*, 295.

[152] Miss H. F. Goodrich, *Brit. Med. J.*, 14 April, 1917, 473.

[153] W. B. Drummond, *ibid.*, 9 June, 1917, 704

[154] *Perf. and Essent. Oil Rec.*, 1916, **7**, 296

PHOTOGRAPHIC MATERIALS AND PROCESSES.

By B. V. Storr, M.Sc

Chemist, Messrs. Ilford Ltd.

Apart from work on the production and perfecting of a satisfactory colour cinematograph process, it is probable that the chief photographic effort in the past eighteen months has been towards the improvement of methods particularly adapted to problems of the war. Exactly what has been accomplished in this direction is not yet disclosed to the general public, although some indications have been given in the form of special photographs such as those shown at the last exhibition of the Royal Photographic Society.

On the whole the general manufacturing conditions have been getting gradually more and more difficult, although in some directions there has been an easement. Bromides, which reached a maximum price of about 25s. per lb. in 1916, have settled down again to about 5s. per lb., while silver, which reached a record price of just over 1s. 6d. per oz. troy, has dropped again to somewhat nearer its normal price. Gold chloride on the other hand has increased in price by about 25 %. Gelatin and all kinds of paper have been getting steadily scarcer and dearer, and owing to their own particular circumstances the manufacturers have found difficulty in maintaining their former standard. The condition of the glass market has compelled manufacturers to make use of renovated negative glass. The general effect of the entry of the United States into the war is not yet fully evident, but it appears highly probable that supplies of some of the raw materials will be still more restricted.

The general position on some smaller though essential points has improved greatly. In addition to metol substitutes, metol itself is now being produced in this country as well as *p*-aminophenol, which latter is also being made in Canada; in Australia[1] the manufacture of pyrogallic acid and amidol has been undertaken by a department of the government. The position in enemy countries is not known with certainty, but the patented process of Pape[2] to resuscitate old developers

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Board of Trade J., Aug. 31, 1916; *J.*, 1916, 944.

Ger. Pat. 295256, 1916; *J.* 1917 238.

by the addition of alkali is suggestive. Schering[3] improves baryta coated papers by a further coating of albumen, and Luppo-Cramer[4] makes the suggestion to improve packing papers by impregnation with manganese dioxide.

The production of sensitising dyes to replace those in general use before the war has been successfully accomplished by W. J. Pope,[5] under whose direction are now being made for Ilford Limited, sensitol red and green (German pinacyanol and pinaverdol) and a new sensitiser, sensitol violet, in addition to erythrosin and a number of dyes used for making photographic light filters. These are being used both in this country and in the United States.[6]

NEGATIVE PROCESSES.

There is little of actual progress to record in negative processes. The attempt to increase the effective speed of X-ray plates is being made in several directions but no serious advance can as yet be reported. Baker[7] increases X ray speed by the use of two intensifying screens, one in front of the film, very transparent to X-rays, and one behind the film less transparent; Edwards[8] for the same purpose proposes to coat celluloid film on both sides with emulsion. Paris and Picard[9] have extended their patent with respect to phosphorescent substances to include the use of phosphorescent zinc sulphide as a substratum screen, a film of gelatinous alumina being precipitated on the sulphide to prevent contact with the sensitive coating.

La Rougery[10] has patented the production of a special negative paper by high-temperature calendering and pressure and Hudson[11] the process of using an ordinary white paper or card for negative purposes, prints being obtained by reflected light. Sosna and Biedebach[12] have extended their list of dyes used to prevent dark-room fog, &c., to include phenolphthalein, which turns red in alkaline developers—a process very similar in principle to the old method of using a dye in the developer.

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[3] Ger. Pat 295502, 1913, *J*, 1917, 306.

[4] *Phot. Ind*, 1916, Heft 43; *Z angew Chem.*, 1917, Ref. 23; *J* 1917, 305.

[5] *J*, 1917, 163.

[6] *Phot J. Amer*, 1917, 419-422

[7] Eng. Pat. 17092, 1915, *J*, 1917, 163.

Eng Pat 111913, 1916, *J*, 1918, 75A.

[9] Addition to Fr Pat 477173, *J*, 1916, 1131.

[10] Eng Pat 108193, 1916; *J*, 1917, 1029.

[11] Eng. Pat 14511, 1915; *J*, 1916, 1536

[12] Ger. Pat. 292723, 1915; *J.*, 1916, 1083.

Several of the processes of manipulation have received considerable attention. Crabtree,[13] of the Kodak Research Laboratory, has a paper on development at high temperatures such as are frequent in tropical countries. The chief hardening agents are formalin, alum, and chrome alum, which may be employed before, during, or after development, the method recommended is to use a p-aminophenol developer, which causes very little swelling of the gelatin, followed by a plain fixing bath, a chrome-alum fixing bath, or a formalin fixing bath according to the temperature In the experiments 95 F (35 C) was taken as the maximum which need be considered. An interesting method of using a two-solution developer is given by North,[14] who treats the plate first with the solution of reducer and then with the alkali, a method which has the effect under suitable conditions of restraining the denser parts of the image and allowing full development of the slight tones. *p*-Phenylenediamine or quinol with ammonium chloride[15] is recommended as developer when fineness of grain is desired, the slight solvent action of these substances on the silver salt assisting in this direction, Koch and du Prél,[16] however, attribute the effect to a development of part only of the silver bromide granule. Brewster[17] patents the use of the same developer, combined with nitrite, for development of a wide range of exposures, both substances were of course known already as preventives of reversal when present in the film during exposure

Ross,[18] for the production of stellar images, recommends the use of a quinol and alkali hydroxide developer as giving clean-cut images, a practice in agreement with that of process workers In this connection some experiments of Campbell[19] and Turner[20] are interesting. The former, by measurements of spectrograms, obtained smaller readings for the separation of pairs of lines than were given by Rowland's tables. The latter got a similar effect in crossed images of a reseau when the lines approached within a certain limiting distance and suggests some mutual effect between the images, it would be interesting to know to what extent this effect could be explained by a disturbance of the mas-centres of slightly separated images by reason of the overlapping o the fringes between them, and also whether an actual slight displacement of the lines towards one another is produced in the drying of the plates by reason of the hardening of the film between the lines as compared with that on either side.

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[13] Communication No. 62 from Eastman Kodak Research Laboratory *B J* 1917, 555-559; *J*, 1918, 21A

[14] *Photography*, 1917, 3-4.

[15] Lumiére and Seyewetz, *Phot. Korr.* *Phot J Amer*, 1916, 406.

[16] *Phys Zeits*, 1916, 536-540. *Sci Abs*, 1917, 53

[17] Eng Pat., 9331, 1915, *J*, 1916, 907

[18] Communication No. 47 from Eastman Kodak Research Laboratory. *B* 1917, 629.

[19] Lick Observ Bull. [No 284], 1916, 28-29. *Sci Abs*, 1917, 19.

[20] Roy. Astronom Soc. M. N. 77, 1917, 519-521. *Sci. Abs*, 1917, 396

Hochstetter[21] has patented a combined developing and fixing bath which contains thiosulphate and glycerin, with citrate apparently as restrainer.

The general question of fixing and washing has been examined by Elsden[22] and Warwick.[23] The former determined the rate of removal of thiosulphate from a gelatin film by successive washings and found no evidence of adsorption. The actual time necessary for complete removal will of course depend upon the amount of thiosulphate present but chiefly upon the rate at which equilibrium is attained between the film and the washing water, this being a function of the nature of the gelatin film and temperature. Warwick found the same general rule to apply and examined also the behaviour of papers, where the absorbent base complicates the problem, and the method of washing in running water. In a further paper Warwick[24] considers the rate of removal of the silver salt by thiosulphate, the normal law being again followed. The rate is dependent on the strength of the hypo solution, a maximum being reached at about 40% and a zero rate at saturation point. He used a silver sulphide test method for estimating the quantity of silver. His general conclusion as to the correctness of the advice usually given to fix for twice as long as is required to "clear" the film is combated by the Editor of the Photographic Journal of America,[25] who found that thorough washing completely removed all the silver from plates taken from the fixing bath immediately all turbidity had disappeared.

Weinhandler and Simpson[26] patent a method of destroying thiosulphate and salts of weak sulphur acids by means of hypochlorite produced by the electrolysis of sodium chloride solution containing prints or negatives.

Bainbridge[27] recommends the permanganate test as the most delicate for thiosulphate, an indication being given by degradation of tint even at a dilution of 1 in 15,000,000; the mercurous nitrate test is more affected by common impurities and indicates only up to 1 in 2,000,000.

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[21] U.S. Pat. 1207142, 1916; *J.*, 1917, 163.

[22] *Phot. J.*, 1917, 90–94; *J.*, 1917, 354.

[23] From *American Photography*; *B. J.*, 1917, 261–4; *J.*, 1917, 669.

[24] From *American Photography*, 1917; *B. J.*, 1917, 617–620; *J.*, 1918, 39A.

[25] *Phot. J. Amer.*, 1917, 171–172.

[26] U.S. Pat. 1224984, 1917; *J.*, 1917, 669.

[27] *Photography*, 1917, 81.

A considerable amount of discussion has centred round the properties of various reducing solutions, a desideratum being a reducer having an effect proportional to the depth of image. Huse and Nietz,[28] following up a suggestion of Deck,[29] examined the effect of combined permanganate and persulphate, and also that of hypochlorite,[30] both reducers being nearly proportional. Becher and Winterstein[31] have examined the action of iodine both alone and combined with thiourea and with cyanide; they give also a general classification of the best known reducers. Greenall[32] examined mixtures of thiosulphate and persulphate, which are much steadier in action than persulphate alone. Gear[33] calls attention to the preserving action of potassium bromide, manna, and glucose on ferricyanide solutions. Smith[34] recommends ammonio-copper sulphate in place of ferricyanide, now that the latter is so expensive.

A paper by Crabtree[35] describes the variation of flash powders with their composition, both as to the metal and the oxidiser used, with the fineness of division of the metal and with the arrangement when fired. A mixture containing sodium oxalate, red phosphorus, a metallic powder such as magnesium or a mixture of magnesium and aluminium, and a substance such as strontium nitrate, is patented[36] by him for the Eastman Kodak Co.

Wedekind[37] has patented the use of metals such as zirconium, thorium, and titanium, mixed with their nitrates or chlorates, for the production of smokeless and odourless flash-powders.

Crowther[38] has examined the chemical reactions involved in the chromium intensification process first suggested by Eder and afterwards modified and expanded by Piper and Carnegie in 1905. With Eder's original formula in which a higher proportion of acid is used than in any of the modifications suggested and which leads to only slight intensification, there does not appear to be any chromium compound attached to the bleached image. In the case of the other three formulæ given by Piper and Carnegie, where the intensification obtained increases as the proportion of acid is reduced, the amount of attached chromium also increases; in the extreme case this appears to be partly chromium hydroxide and partly chromium trioxide, the latter imparting a brown colour, and in the other cases only the hydroxide.

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[28] *J. Franklin Inst.*, 1916, 532–533; *B. J.*, 1916, 580–582; *J.*, 1916, 1180.
[29] *B. J.*, 1916, 391–392.
[30] *B. J.*, 1917, 143.
[31] *Z. wiss. Phot.*, 1917, 1–16; *J.*, 1918, 10A.
[32] *Photography*, 1917, 205.
[33] *Phot. J.*, 1916, 184.
[34] *B. J.*, 1916, 574.
[35] *B. J.*, 1917, 29–32.
[36] U.S. Pat. 1240027, 1917; *J.*, 1917, 114A.
[37] Ger. Pat. 293998, 1914; *J.*, 1916, 1180.
[38] *J.*, 1916, 817.

POSITIVE PROCESSES.

The supply of platinum is still too limited for it to be available for photographic purposes. General Thayer[39] is said to have discovered a considerable source of it in the Adirondacks, but that has not yet materialised. The Platinotype Company have introduced "Palladiotype" in which palladium is used to give effects very similar to those of platinum, and the use of palladium as a toning agent for collodion paper facilitated by a bath which contains ammonium chloride, sodium glycollate, and succinic acid and does not require a special fixing bath, has been recommended by Valenta.[40] The latter has also investigated the properties of salts of diglycollatoferric acid[41] from which an excellent blue printing paper can be obtained, but of poor keeping qualities. Valenta[42] also draws attention to the fact that Sulzberger's patent on the use of ferrocyanide (mentioned in the last report) was forestalled by Fox Talbot in 1839 and that the process was mentioned in Eder's Handbuch.

Strasser[43] has worked out a toning method with the use of Schlippe's salt; Schering[44] has improved his original selenium toning bath. Nietz and Huse[45] have worked out in some detail the possibilities of obtaining sepia tones by the use of strongly restrained developers. Very few papers give good tones by this process; the best results are obtained by a chloro-quinol developer containing bromide and metabisulphite and necessitating an increase of exposure of from 75 to 100 times that required by normal developers.

Spitzer and Wilhelm[46] have patented a combined toning and fixing bath containing tellurous or telluric acid or their salts along with thiosulphate.

Two patents for transfer processes have been brought out, one by

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[39] *Phot. J. Amer.*, 1917, 480.

[40] From *Phot. Korr.* *B. J.*, 1917, 80.

[41] From *Phot. Korr.* *B. J.*, 1917, 79.

[42] From *Phot. Korr.* *B. J.*, 1917, 81; Ann. Rep., 1, 302.

[43] *Phot. Rundsch.*, 1916, 33–35. *Chem. Zeit.*, 1916, Rep. 304; *J.*, 1916, 1035.

[44] Ger. Pat. 296009, 1914; *J.*, 1917, 615.

[45] Communication No. 53 from Eastman Kodak Research Laboratory, *B. J.*, 1917, 497–499; *J.*, 1918, 21A.

[46] Ger. Pat. 292352, 1914; *J.*, 1916, 1083.

Pin[47] for film in which coconut oil soap is the chief stripping agent, and one by Kent and Middleton[48] for paper, using paraffin wax. A transferotype bromide paper on similar lines has been introduced by the Kodak Co.

In process and allied work, Bull, Smith, and Turner[49] have a paper on some of the intricacies of the half-tone process, Fishenden[50] on the photographic engraving of rollers for intaglio printing, and Crabtree[51] on the advantage of using citric and oxalic acids respectively in the preparation of zinc and aluminium plates for lithographs. Doran[52] has patented the use of a half-tone screen composed of small lenticular grains, preferably coloured (see also Knudsen, Ann. Rep. **1**, 303). Rieder[53] obtains an intaglio printing surface by forming a screen surface in bichromated fish glue and getting a positive over that in caoutchouc and asphalt; Orans,[54] for ease of correction, prints on emulsion coated on a serrated surface of the type of a Levy screen on celluloid or celluloid on glass.

Meadway[55] uses a mixture of naphthalene and a white metal, with rubber as adhesive, as coating for a projection screen, while Bebbington[56] coats a support such as glass, gelatin, or waxed paper with a dull blue-coloured solution and projects on to that side, the audience facing the other side.

An interesting account is given by Warbarg[57] of the work of Meissling on the use of dyes such as erythrosine and auramine as hardening agents in the carbon and gum processes, an effect which is attributed to the formation of formalin. The erythrosin preparations are said to be quite equal to those containing bichromate and to have better keeping qualities.

COLOUR PROCESSES AND CINEMATOGRAPHY.

Three-colour cinematograph methods have been produced in America. The Technicolor[58] process, introduced by a company formed to work

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[47] U.S. Pat. 1184772, 1916; *J.*, 1916, 755.

[48] Eng. Pat. 12091, 1915; *J.*, 1916, 1035.

[49] *Phot. J.*, 1917, 8 14; *J.*, 1917, 353.

[50] *B. J.*, 1916, 431–433.

[51] Communication No. 48 from Eastman Kodak Research Laboratory; *J. Franklin Inst.*, 1917, 635–636; *J.*, 1917, 668.

[52] Eng. Pat. 7540, 1915; *B. J.*, 1916, 410.

[53] Eng. Pat. 8357, 1914; *J.*, 1916, 754.

[54] Eng. Pat. 16040, 1915; *J.*, 1916, 755.

[55] U.S. Pat. 1216154, 1917; *J.*, 1917, 403.

[56] Eng. Pat. 104711, 1916; *B. J.*, 1917, 251.

[57] *Amato-Photographen*, Jan., 1917; *B. J.*, 1917, 96; *J.*, 1917, 354.

[58] *B. J.*, 1917, *Colour Supplement*, 41–43.

the Comstock patents, is a two-colour additive method, the images being superposed on the screen. The taking apparatus is a single lens camera with a special form of grid mirror for division of the light; the projection camera includes as a registering device two refracting plates, one in each beam, and pivoted on axes at right angles. The Prizma[59] process of the Panchromotion Co., based on the patents of Wohl and Mayer and Kelly and Raleigh, uses four overlapping colour filters in the taking camera and in the projection camera has two main filters each with smaller sections of a different colour inserted – an orange-red with magenta segments and a blue-green with blue segments. The full details of the third process[60] are not to hand but it would appear to have been brought out by the Eastman Kodak Co. It uses a two-colour single film positive, with the colours on opposite sides of the same film. The printing is done from a colour selection negative with two alternating sets of pictures, a device of lenses and prisms projecting at the same time images of two consecutive pictures one on either side of the positive, each side of which is stained to prevent action of either light on both films.

A large number of patents have been taken out for various details in connection with colour processes. One of the most interesting is that of Szczepanik and Habrich[61] for the bleach-out process, applied for in 1913; particulars are given of the dyes and sensitisers used. Gartlgruber[62] covers a stereoscopic process in which the pairs of pictures are in complementary colours. Henley[63] has a method of stereo-cinematography, using two taking cameras and two negatives from which a single positive is obtained; a special viewing apparatus is required. Wilkinson,[64] Jones,[65] Ives,[66] Hess,[67] and Fox[68] (with Kinemacolor) al use variations of very similar methods of obtaining and combining two or three colours in printing. The Brewster Film Co.[69] uses an adsorbent silver halide, formed by the action of a halogen and a halide such as iodine in potassium iodide. Christensen[70] extend his method of taking advantage of variations in the porosity of a developed film, to the use of special filling substances in the fixing bath. Thornton[71] has several patents in connection with the printing of positives, including the use of a photo-mechanical printing film and special devices for registering films in printing. Shorrocks[72] has a method of staining in two colours at one operation; a film with two sets of alternating pictures, one of which sets has been bleached, is passed through a bath containing a dye such as rhodamine, which stains the bleached pictures red, and ferricyanide citrate, which stains the unbleached pictures blue-green.

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[59] *B. J.*, 1917, *Colour Supplement*, 14.

[60] *B. J.*, 1917, *Colour Supplement*, 45–46.

[61] Eng. Pat. 20396, 1916; *B. J.*, 1916, *Colour Supplement*, 45–47.

[62] Eng. Pat. 104069, 1916; *B. J.*, 1917, 251.

[63] Eng. Pat. 106373, 1916; *B. J.*, 1917, 439.

[64] *B. J.*, 1916, *Colour Supplement*, 26–27.

[65] Eng. Pat. 105380, 1916; *J.*, 1917, 675.

[66] U.S. Pats. 1188939, 1916, and 1247116, 1917; *J.*, 1916, 907, and 1918, 40A.

[67] U.S. Pat. 1225246, 1917; *J.*, 1917, 669.

[68] U.S. Pat. 1207527, 1916; *J.*, 1917, 163.

[69] Eng. Pat. 100098, 1915; *B. J.*, 1917, 303 and 304. U.S. Pat. 1214940, 1917; *J.*, 1917, 403.

[70] Fr. Pat. 481149, 1916; *J.*, 1917, 64. Eng. Pat. 103890, 1916; *J.*, 1917, 354.

In the making of multicoloured screens, Pierman[73] has a process of weaving coloured transparent threads, Schleussner[74] uses a single layer of particles, coalescence being produced by exposure to a solvent vapour, Kitsee[75] obtains very fine particles by spraying a solution of a colloid into a hardening or coagulating vapour, *e.g.*, gelatin into formalin, and Tarlton[76] gets a two-colour screen by a first coating in one colour of a single layer of particles, coating over this with a stained bichromate film, exposing through the back, and developing, which leaves the interstices filled with the second coating.

Walker,[77] for the Hess Ives Corporation, uses a reflecting mirror coated with a dichroic compound such as eosine; there is an appreciable gain in the total amount of available light compared with the normal reflecting mirror which cannot utilise more than 50% of the two component lights.

Miss Greene,[78] Hochstetter and Pierson,[79] and Trivelli[80] have patented various methods of renovating cinema films, the two former by mechanical means, the last by means of a lacquer. Ives[81] protects the sensitive surface of the film by a varnish of gum damar, removed before development. Lovejoy,[82] for the Eastman Kodak Co., uses a composite base, the parts of which are oppositely electrified by friction, thus avoiding the dangers from this source in the handling of sensitised films. Planchat[83] dries cinema film by the pressure obtained by passing it through a column of mercury.

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[71] Eng Pats 5100, 1915; 8300, 1915, 100629, 1916, *B. J.*, 1916, 587, 1916, 907.

[72] Eng Pat 111054, 1917; *J.*, 1917, 1290.

[73] U.S. Pat 1196718, 1916; *J.*, 1916, 1035.

[74] Ger. Pat. 293004, 1914; *J.*, 1916, 1083.

[75] U.S. Pat. 1206000, 1916; *J.*, 1917, 101.

[76] Eng. Pat 110993, 1917; *J.*, 1917, 1290.

[77] Eng. Pat. 110089, 1917; *J.*, 1917, 1195.

[78] Eng. Pat. 14095, 1915; *B. J.*, 1916, 561.

[79] U.S. Pat. 1192424, 1916; *J.*, 1916, 944.

[80] Eng. Pat. 7956, 1915; *J.*, 1916, 754.

[81] U.S. Pat. 1240344, 1917, *J.*, 1917, 1148.

[82] U.S. Pat. 1232702, 1917; *J.*, 1917, 1065.

Theoretical and Experimental.

The subject of the nature of the latent image has been approached from several standpoints Channon[84] gives an account of some experiments extending over a period of twenty years, showing the effect of time on the latent image, loss of density and veil are the chief effects, there was also some evidence of photo-retrogression in several of the experiments Homolka[85] discusses the difference between ferricyanide and reducing substances such as ferrocyanide, sulphite, and phenylglycine in their effects when plates containing them are exposed to light There is no visible action in the one case and a blackening in the others, and Homolka uses this result to support the subbromide and perbromide, formation theory (See also a further paper by Crowther[86] on the use of substituted p-phenylenediamines.) On the other hand Padoa and Mervini,[87] from their work on temperature coefficients, conclude that the formation of a latent image is not due to a decomposition of the order $AgCl \quad Ag + Cl$.

Several interesting papers on the properties of gelatin and its solutions have appeared. Moeller[88] gives an account of some experiments showing the laminated structure of jellies and supporting the theory of the fibrillated structure of gelatin. Arisz[89] has studied the viscosity of solutions of gelatin in a glycerin-water mixture and its variation with temperature, concentration, etc. He finds permanent loss of viscosity above 65 C, due to partial hydrolysis Below this point the change of viscosity with temperature appears to be dual in nature; there is the change produced merely by alteration of temperature such as is shown by all ordinary liquids, and the change produced by alteration of structure. The latter is, especially at low temperatures, much greater than the former, and occurs much more slowly. There is for any temperature above the setting point an equilibrium viscosity, which is, however, diminished at low temperatures by stirring. The Tyndall effect was also examined and the curves connecting this and temperature, as well as the curves for viscosity, were found to be quite continuous, with no break at the setting point. These results are quite in agreement with some obtained in the Ilford laboratories with aqueous solutions, which showed from a study of viscosity and of melting and setting points that the properties of a jelly as well as those of a liquid gelatin solution are dependent on its previous history and the rate of attaining equilibrium is much decreased with lowering of temperature, observations on an industrial scale have also shown that the same is true of dry gelatin film, the properties of which depend both on the condition of the solution from which it is made and on the conditions of drying. The patent of Ilford Limited with Renwick and Storr[90] for the recovery of silver from weak gelatin emulsions is also of interest in this connection, one of the methods used depends apparently on the interaction between the gelatin network and a colloidal hydroxide formed by the dilution of a metallic salt in a slightly alkaline bath, the reaction not taking place with a perfectly fresh gelatin solution nor above certain limiting temperatures.

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[83] U S Pat 1262077, 1917, *J*, 1917, 943

[84] *Phot J*, 1917, 72-84, *J*, 1917, 354

[85] From *Phot Korr*. *B J*, 1917, 84.

[86] *J*, 1916, 817-820

[87] *Atti R Accad Lincei*, 1916, ii, 168 171; *J*, 1917, 47

[88] *Koll Zeits*, 1917, 257-270, *J*, 1917, 1186.

[89] *Kolloid Chem Beihefte*, 1915, 1 90, *J Soc Leather Trades Chem.*, 1917, 50-51, *J*, 1917, 1243-1244

Biltz, Bugge, and Mehler[91] have studied the osmotic pressure of various gelatin solutions and arrive at some conclusions as to molecular weight and complexity. They compare also, for various gelatins viscosity and gold value (the amount of gelatin solution required to protect a standard colloidal gold solution against precipitation by certain reagents).

Hodgson[92] has published a paper on the physical properties of plate grains, in which some excellent photomicrographs are given in illustration. There is generally a change of shape and an increase of size of grain on development, though occasionally the shape is retained; cases were also found in which development of a grain started from several nuclei. It would be interesting to know the reasons for his conclusion that the silver halide grains are tetrahedra for silver bromide and silver iodide are both dimorphous (cubic and hexagonal), the latter being hexagonal at normal temperatures, the former either cubic or hexagonal, in the form of hexagonal or triangular laminæ. The "feeler" phenomenon previously observed by Scheffer was noticed only once, and then under such conditions as to suggest an entirely different explanation from that advanced by Scheffer, and having no reference at all to the nature of the latent image. Koch and du Prel,[16] in the investigation already mentioned, also made a microscopical examination of silver bromide grains in various photographic plates, and the effect on them of exposure, development, and fixing.

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[90] Eng Pats 16708 and 102168, 1913, J, 1917, 47

[91] Z. physik Chem, 1916, 705 712. Z. angew. Chem, 1916, Ref, 540; J 1917, 47

[92] Communication No 56 from Eastman Kodak Research Laboratory; B J 1917, 532-534, J., 1918, 20A.

Saegusa,[93] in some work in the crater of a volcano, obtained reversal which he succeeded in tracing to sulphur dioxide; the effect was only temporary, disappearing if the plates were kept several days. He has examined also the varying effects of different coloured lights,[94] and their combined effects on photographic plates; he does not appear to have found any evidence of the antagonism of different colours.

An important contribution to the general subject of photometry is the paper of Renwick[95] on tone reproduction. By a careful consideration of the curves of sensitiveness of both plates and papers he indicates to what extent it is possible to obtain a print having the same gradation as the original, and also the possibilities of compensating for the errors of the negative by the qualities of the printing paper. The general question as to what relationship it is desirable to have between the scale of tones of the original and that of the reproduction, a problem which introduces both physiological and psychological phenomena, also receives consideration. A number of data are collected and arranged respecting range of vision, degree of visibility contrast, etc., at varying degrees of luminosity, and their bearing on the subject discussed along with that of the methods ordinarily adopted by artists.

Bloch[96] has studied the possible variations which may occur in the values obtained for the H. & D. speed number of a plate with variations in the conditions of experiment. He made exposures both with an intensity scale (wedge-screen) and a time scale (sector wheel) avoiding intermittency error in the latter case by using only one slow revolution of the wheel, which was driven by clockwork. The factor actually required to arrive at the value of $\log i$ are the composition o the developer, the γ (degree of development) reached, the value of q (i Schwarzschild's rule, $I^q t = I_1{}^q t_1$, for equal densities), the nature of th exposure (time scale or intensity scale) and the actual values of time an intensity. The variation of speed with developer is considerable, orto giving the highest number and glycin the lowest of those examined and the variation with γ is very marked in some cases, especially with high-speed plates having long under-exposure curves. With such plates it is quite common with normal development (*i.e.*, to a γ of about 1) to obtain a straight-line curve for the whole of a normal range of exposures; if development is carried far enough, however, the normal curve becomes evident. A speed number obtained from the first curve, which more nearly represents the working speed of the plate, is much higher than the true H. & D. speed number obtained from the second curve. One case also is mentioned in which Schwarzschild's rule was not obeyed.

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[93] *Math. Phys. Soc., Tokyo, Proc.*, 1917, 56–63. *Sci. Abs.*, 1917, 223.

[94] *Math Phys. Soc., Tokyo, Proc.*, 1917, 178–185 *Sci. Abs.*, 1917, 561.

[95] *Phot. J.*, 1916, 222–238; *J*, 1916, 1272.

[96] *Phot. J.*. 1917. 51–61; *J.*, 1917, 353.

Padoa and Mervini[96] have determined the temperature coefficients of sensitiveness of various plate emulsions and of citrate paper emulsions for a range of lights of different colours. The former are the same (1·05) for all the colours tested (red, yellow-green, violet, and white) but the latter with white, blue, and ultra-violet light are 1·16, 1·19, and 1·07 respectively.

Hodgson[97] has made a preliminary investigation into the speeds of plates to X-rays. The subject presents some special difficulties because of the fluctuating and intermittent nature of the radiation as ordinarily produced and the results obtained were only intercomparable, no definite standard of exposure being suggested. To avoid the intermittency difficulty the moving-plate exposing device of Jones was used and a steady output of X-rays was obtained by the use of a Coolidge tube. The curves obtained differ from the usual light speed curves in being more hyperbolic in shape, neither straight-line nor over-exposure periods being evident.

Goldberg[98] has determined the tendency to halation by measurement of the fog produced on a protected part of a plate surrounded by exposed parts, making at the same time a comparison wedge-screen exposure. He has also studied the anti-halation effects of various suggested remedies and confirms the prevalent conception that a coloured film between the sensitive film and support is the most effective. Goldberg (*loc. cit.*) also suggested an improvement in Martens's photometer, replacing the usual powerful lamp by a small glow lamp under the photometer table, the method has been tried in the Ilford laboratories with a decided improvement in the range of the instrument.

Hitchins and Gilbert[99] give a detailed description of the development thermostat in use in the Ansco Research Laboratory. It is on a comparatively large scale and electrically heated and controlled. The developing vessel is an arrangement of two concentric cylinders, the developer being circulated by means of a pump from inside to outside of the inner cylinder, on the outer face of which the plates are suspended.

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[97] Communication No. 63 from Eastman Kodak Research Laboratory. *B. J.*, 1917, 654–657; *J.*, 1918, 39A.

[98] Ver. deut. Chemiker, Oct., 1916. *Z. angew. Chem.*, 1916, 394; *J.*, 1916, 1236.

[99] *Phot. J. Amer.*, 1917, 149–153.

Luckiesh[100] suggests the use as a correction filter in spectrographic work of a spectrogram placed in correct position on the plate during exposure. Hodgson and Wilsey[101] have calculated the actual density required at any point of such a filter, given the light intensity and the speed of the plate at that point. The device suffers, however, from the defect in grating instruments that the effect of scattered white light becomes much more pronounced, especially on the thinner parts of the filter, and for that reason it was abandoned in the Ilford laboratories in favour of a colour correction filter placed between the source of light and the slit.

The adaptability of the eye to varying degrees of illumination has been studied in some detail by Nutting[102] and Reeves[103] of the Eastman Kodak Co. They have made quantitative estimations of the retinal sensitiveness under different conditions and of the variation in pupillary area. The former is much the more important in enabling the eye to accommodate itself to extremes of luminosity, the total range being about 1 to 1,000,000; accommodation is much more rapid in going from a weak light to a strong light than in the reverse process. The range of pupillary area is about 1 to 16, and accommodation if made in this respect almost instantaneously.

Wood[104] has obtained photographs of Jupiter and Saturn through infra-red, ultra-violet, yellow, and violet filters. He used for the ultra-violet filter bromine vapour 5 cm. in thickness with a thin filter of potassium chromate.

A very full description is given by Eder[105] of some of the newer sensitising dyes, including dicyanin A, which sensitises to the red and infra-red as far as $850\mu\mu$, pinachrome blue and violet, and pinacyanol green, with their sensitising properties and methods of use. Dicyanin

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[100] *Astrophys. J.*, 1916, 302–309 *Sci Abs*, 1916, 387

[101] Communication No 42 from Eastman Kodak Research Laboratory *Phot J Amer.*, 1916, 406

[102] *B. J*, 1916, 648.

[103] Communication No. 52 from Eastman Kodak Research Laboratory, *B J*, 1917, 415–417.

[104] *Astrophys. J.*, 1916, 310–319. *Sci Abs*, 1916, 383.

[105] From *Phot. Korr*, *B J.*, 1917, *Colour Supplement*, 8.

A was used by Meissner[106] for the preparation of red- and infra-red-sensitive plates in his examination of the spectral lines of a number of different elements in this region.

The effect of β-particles from radium A on photographic plates has been examined by microscopic methods by Ikeuti,[107] continuing the work of Kinoshita and Ikeuti, on lines very similar to those of Sahni (see *Ann. Rep.*, **1**, 314).

Colour photographs have been taken by Nichols[108] of the phosphorescence of metallic sulphides; he submitted the sulphides to a strong intermittent illumination and examined them in the intermittences. Interesting photographs have been obtained by Hyde[109] and by Wilson[110] of air-waves and moving projectiles.

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[106] *Ann. d. Physik*, 1916, 50, 6, 713—718; *Sci. Abs.*, 1917, 97, 8.

[107] *Phil. Mag.*, 1916, 129—131; *Sci. Abs.*, 1916, 395.

[108] *Am. Phil. Soc. Proc.*, 1916, 494—502; *Sci. Abs.*, 1917, 55.

[109] From *Scientific American*; *B. J.*, 1916, 492—493.

[110] From *Camera Craft*; *B. J.*, 1916, 596—597.

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ERRATA IN VOL. I.

Page 129, lines 4 and 5. For [illegible] read formaldehyde.

Page 129, lines 11, 12 and 13, should read: "[illegible] 70 % yield of sodium formate is obtained from [illegible] by passing simultaneously hydrogen and carbon dioxide both under [illegible] atm. through a solution of borax of similar strength in presence of the same amount of the catalyst, at 70° C."

Page 239, lines 5–9, should read: "W. Wöllmer finds that α bitter acid (humulone) by the action of sodium hydroxide yields humulinic acid, which he shows to have the composition C [illegible] H [illegible] O [illegible], besides acetic acid, a saturated acid C [illegible] H [illegible] O [illegible], and isobutyraldehyde. It is considered probable that the aldehyde is formed when wort is boiled with hops."

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